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FUEL-GRADE ETHANOL RECOVERY BY SOLVENT EXTRACTION. TECHNICAL

PROGRESS REPORT

For Period September 15, 1980 through September 15, 1981

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2EHOH	=	2-ethylhexanol
NDD	=	n-dodecane
HDEHP	=	di(2-ethylhexyl) phosphoric acid
TDOH	=	tridecanol
UNFOH	=	Umbrex-N- fatty alcohol
DEHEHP	=	di(2-ethylhexyl) 2-ethylhexyl phosphonate
TBP	=	tri-n-butyl phosphate
DBBP	=	Dibutyl butyl phosphonate
TLA	=	trilaurylamine
TLAO	=	trilaurylamine oxide
2EHOOH	=	2-ethylhexanoic acid
3HPOH	=	3-heptanol
NBUAC	=	n-butyl acetate
DNEHP	=	dineopentyl-2-ethyl hexyl phosphonate
D_e	=	distribution coefficient for ethanol either as concentration or weight ratios
D_w	=	distribution coefficient for water either as concentration or weight ratios
X_e	=	weight fraction ethanol in the raffinate.
X_w	=	weight fraction water in the raffinate
Y_e	=	weight fraction ethanol in the organic phase
Y_w	=	weight fraction water in the organic phase
S	=	ethanol-to-water selectivity = D_e/D_w

Fuel-Grade Ethanol Recovery by Solvent Extraction:

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ABSTRACT

Experimental and computational analyses suggest that liquid/liquid extraction represents a technically feasible alternative to distillation for the recovery of fuel-grade ethanol from dilute aqueous mixtures. The class of high boiling aliphatic alcohols contains several species which are available commercially for around 50 cents per pound in bulk volume and that represent useful extractants when properly blended. Suitable blending agents include the class of inexpensive, normal paraffinic refinery products such as NORPAR-12 and branched paraffinic cuts like ISOPAR-G. Chlorinated diluents, such as tetrachloroethane, greatly increase the solvent selectivity, but they are probably not usable as diluents due to their relatively high toxicities and volatilities. The experimental data also suggest, however, that 10 vol % dodecyl alcohol in NORPAR-12 will recover a 98 wt % ethanol product from an aqueous phase containing ethanol concentrations as low as 15 wt %. Twenty vol % tridecyl alcohol in NORPAR-12 will recover a 98 wt % product from ethanol concentrations as low as 10 wt % and 50 vol % tridecyl alcohol in tetrachloroethane will recover a 98 wt % ethanol product from ethanol concentrations as low as 5 wt %. Each recovery system requires only one solvent extraction cycle followed by a vacuum stripping step to isolate the ethanol product. Experimental data are presented for 28 candidate solvent extraction systems.

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1 INTRODUCTION

The goal of this program is the development of a cost-effective and energy-efficient liquid/liquid solvent extraction process which can recover fuel-grade ethanol from dilute fermentation liquor (about 10 wt %ethanol or less). In this case, "fuel-grade" refers to ethanol mixtures containing roughly less than 2 wt % water which do not form a second aqueous phase when mixed in a 9 to 1 gasoline-to-ethanol product volume ratio. Gasahol products made from ethanol feedstocks containing at least 98 wt % ethanol do not form water hazes when they are diluted with straight unleaded gasoline. This physical property is a very important one which is generally not exhibited by gasahol mixtures which are made from less than fuel-grade ethanol feedstocks.

On the other hand, a low-grade ethanol feedstock, say 90-95 wt % ethanol, may be recovered from a single solvent extraction cycle and used to produce a low-grade gasahol product without achieving a fuel-grade quality in the ethanol feedstock beforehand. Moreover, this option is intriguing because it could yield substantial energy saving in gasahol production, but it may also require the subsequent addition of a gasahol modifier to prevent water haze formation whenever the gasahol is diluted with straight gasoline. Also, any such modified gasahol products will require a careful evaluation of their motor characteristics as well as the cost of the modifier.

In addition, any viable liquid/liquid solvent extraction process must permit solvent recycle with low solvent losses and make-up costs in order to compete economically with distillation techniques.

The solvent toxicity both to the general environment and any micro-organisms that may be used to produce the dilute fermentation liquor, the feed to the recovery process, are also important economic factors. This aspect of the problem, however, is currently beyond the scope of the research program. The toxicity question may be addressed more properly in the third year of this study after a basic recovery process has been demontrated on an integrated, bench-scale basis.

Previous studies at Georgia Tech (1-4) resulted in several processing concepts for ethanol recovery that involve continuous fermentation, solvent extraction, and several alternative solvent stripping steps. The initial case study (1) indicated that recovery costs might be reduced by as much as 40 % when compared to a vacuum fermentor and conventional fractionator combination (5) that produced the 95 % azeotrope. The projected savings are greater, however, when the comparisons (8,9) include the benzene drying step. Also, the initial case design basis assumed an organic-to-aqueous volumetric flow ratio of about ten-to-one which now appears overly conservative.

On the other hand, it may be necessary or desirable in some cases to design a two-cycle (6) process for recovering fuel-grade ethanol feedstock for gasahol production. In these cases, the first cycle would be operated primarily to achieve a high ethanol recovery while

discharging the bulk of the water as either a waste stream or else to the fermentor as recycle. The second cycle would be operated primarily to dry the final product to "fuel-grade" levels and the raffinate from this latter step would be recycled to the first recovery cycle in order to limit ethanol losses. Alternatively, the second cycle may consist of the actual gasahol production step and a modifier addition if a low-grade ethanol feedstock is produced by the first recovery cycle.

The Georgia Tech processes are based upon the primary assumption that a solvent phase exists which consists of one or more chemical species that are high-boilers, relative to ethanol, and that can be reasonably used to separate ethanol from water. Under these conditions, the resulting clarified extract can then be stripped of its ethanol content by vacuum distillation, for example, with the solvent recycled to the extraction cascade. The ethanol vapors which are produced by stripping must then be condensed to yield the final ethanol product and a reflux stream, if it is needed, which may be sent back to either the recovey or drying cycles. Thus, the two-step process of first extracting the ethanol away from the water, and then stripping it from the solvent, avoids the use of a reboiler as is found in distillation. On the other hand, the vapor condensation step may require refrigeration and, therefore, electrical or mechanical-shaft work.

In principle, the Georgia Tech recovery processes may also be used with continuous fermentors. In this case, there is recycle between the fermentors and the first solvent extraction cascace. In particular, the extraction cascade receives a clarified liquor from the fermentors and

returns its raffinate to the fermentors. Since the raffinate is contaminated with solvent, the solvent cannot be highly toxic to the yeast and the extent to which solvent decontamination is required in order to maintain the viability of the ethanol-producing micro-organisms has not been clearly established at this time. However, limited studies with similar solvent systems have been carried out by researchers at Penn State (7).

Assuming that any toxicity effects due to the solvent can be overcome, then there are at least three favorable synergisms between the fermentation process and the recovery process. First, since the raffinate is a feed to the fermentor rather than a waste, the optimal alcohol levels are reduced. This effect makes the recovery step more energy-efficient. Second, the solvent extraction cascade can be operated so that the optimal ethanol concentrations in the fermentor can be maintained. This effect makes the fermentor more efficient. Third, the solvent losses from the extraction process are reduced by the fermentor since the clarified liquor entering the recovery process as a feed is already nearly saturated. This effect tends to decrease solvent losses both by entrainment and solubility. Thus, the habitual recycle between these two processing steps is envisioned to have favorable effects on the overall production system that neither subsystem has alone.

2   EXPERIMENTAL

The experimental efforts have focused on the identification of a
solvent system with suitable physical properties for use in large-scale
commercial recovery systems. In this regard, one important constraint
is the solvent cost (hopefully around 50 cents per pound) and, secondly,
its level of chemical toxicity. The first constraint limits practical
extractants to substances that are available in bulk quantities as
chemical intermediates. The second constraint may preclude the use of
halogenated substances, such as tetrachloroethane or chloroform, that
are relatively dry, but also toxic. Because of the relative selectivity
of chlorinated solvent modified systems; however, high-boiling species
which are commercially available may be attractive for some
applications.

2.1 Scouting Tests

In order to rapidly evaluate alternative extraction systems,
several simple "scouting" procedures have been used. A few milliliters
of the candidate extractant and a water-ethanol mixture are placed in
separate test tubes. Their respective indices of refraction are then
measured. Subsequently, the organic and aqueous volumes are
equilibrated in a test tube by vigorous shaking for about one minute.
The two phases are then allowed to separate and are centrifuged if

necessary. Any apparent changes in the organic and aqueous volumes, the refractive indices for both phases, and any other factors (e.g. a persistent haze) are then noted.

A useful candidate extractant will usually show a decrease in the organic and aqueous phase refractive indices upon equilibration. These changes suggest that a preferential extraction of ethanol has occurred. In addition, a useful extractant system will probably exhibit some increase in organic volume upon equilibration. Other conclusions, however, can be drawn from such a test and these are summarized in Table 1. Table 2 summarizes the results of scouting tests that have been performed for several candidate extractants.

Another simple scouting test consists of equilibrating known weights (typically, three to five milliliters of each phase) of solvent and an aqueous ethanol phase. In this case the weight percentage of ethanol in the aqueous phase is measured using GC analysis before and after equilibration. Subsequently, the aqueous phase is removed from the sample vial using a syringe. The residual organic phase is weighed and the apparent ethanol distribution coefficient may be determined from the ethanol material balance.

If the water distribution coefficient is determined in this manner, however, the technique may result in negative values because of the inaccuracy of physically separating the two phases and the relatively small value of the water distribution coefficient. On the other hand, the method may be improved by also chromatographing a sample of the

Table 1. Commonly observed refractive changes during scouting tests.

| Case | Refractive Index Changes[a] | | Conclusions |
	Aqueous	Organic	
1	0	0	No phase transfer occurred
2	0	−	Equal amounts of water and alcohol extracted
3[b]	−	−	More ethanol than water extracted
4[c]	+	−	More water than ethanol extracted and/or the solvent is water soluble
5	+	0	The solvent is water soluble, but does not extract

[a]All cases are subject to cancellation of changes, or else change reversals, due to high solvent solubilities in the aqueous phases. In these cases, the aqueous phase is hazy after equilibration or else becomes hazy when it is subsequently diluted with water.

[b]This is the most favorable case.

[c]This case is ambiguous.

Observations	Conclusions
phases clear, rapid disengagement	negilible phase transfer
phases slightly hazy gagement in about 5 min.	more water than ethanol extracted and/or the solvent is noticesbly water soluble
	more ethanol than water extracted
lifuged to form a hazy organic and aqueous phase	" " " " "
phases hazy, disengaged in 10 min.	more water than ethanol extracted and/or the solvent is notic ibly water soluble
lear phases	more ethanol than water extracted
aqueous, clear organic	" " " " "
organic clear aqueous	" " " " "
aqueous, clear organic	" " " " "
d three phases	inappropriate extractant
	more water than ethanol extracted and/or the solvent is noticably water soluble
	more ethanol than water extracted
ifuged to give two clear phases	" " " " "
ifuged to give clear organic and aqueous phase	" " " " "
ifuged to give two slightly hazy phases	" " " " "
iguged to give two clear phases	" " " " "
ifuged to give two clear phases	" " " " "
lear phasees, rapid disengagement	" " " " "
ifuged to give clear phases	" " " " "
ifuged to give two clear phases	" " " " "
	" " " " "
	" " " " "
	" " " " "
	more water than ethanol extracted and/or the solvent is noticeably water soluble
	more ethanol than water extracted

ganic volume.

organic phase and then calculating the ethanol-water separation factor on a solvent-free basis. In this case, it is impossible to calculate a negative water distribution coefficient, but the method may still suffer from its adverse effects on the baseline of the GC instrument.

Table 3 summarizes several single point distribution coefficients for ethanol extraction that have been calculated. Solubility curves and additional tie lines have not been measured for most of these systems.

Table 3. Single-point GC Test Results

| Solvent System | Equilibrium Conditions | | | |
	Aq Wt[a]%	D_E	D_W	SF
50 vol% trido decylamine oxide in NORPAR-12	15.0	0.046	0.0031	15
50 vol% 2-methoxyl phenol in ISOPAR-G	Formed Three Phases			
50 vol% 2-ethylhexanol in Chloroform	22.0	0.75	0.058	13
50 vol% methyl ethyl ketoxime in NORPAR-12	12.9	0.45	0.26	1.7
HMW Conoco diol	8.8	0.51	0.018	28
LMW Conoco diol	9.1	0.51	0.019	27
100% Chloroform	4.0	0.28	0.019	14

[a]Initial aqueous weight percentage was 15.5% ethanol.

The GC analysis was performed using a Hewlett Packard 5710A GC with a four-foot-1/8 inch diameter Porapak Q 80/100 mesh column operated at 140 degrees Centigrade and using helium as the carrier gas. Ethanol and water standards were used to determine the weight percentage ethanol as a function of the area precentage of ethanol associated with the ethanol and water peaks only (i.e on a solvent-free basis). A nearly linear relationship was found to exist.

Peak integration was performed using a Hewlett Packard 3390A peak integrator. The reproducibility of successive injections was such that variations usually occurred only in the third significant figure of the ethanol area percentage. When organic samples were injected, it was usually necessary to cycle the GC to an operating temperature of 250 degrees Centigrade in order to drive the solvent off of the column. Otherwise, the GC would exhibit excessive baseline drift and the area percentages associated with water and ethanol would not always be reproducible.

2.2 Mutual Solubility Curves and Tie Lines

A synthetic method (10) may also be used to determine the distribution coefficients of etharol and water. In this case, the mutual solubility curve is obtained by the titration of cloud points. Successive quantities of either water and ethanol or else solvent and ethanol are added to induce and remove turbidity from either the

saturated organic phase or else the saturated aqueous phase
respectively.

Given the mutual solubility curve, then ethanol distribution
coefficients may be determined from knowledge of the ethanol weight
fraction in the feed and the equilibrium ethanol weight fraction in the
aqueous product. Experimentally, these quantities are conveniently
determined by a GC analysis of the aqueous ethanol and water mixture
before and after it is equilibrated with the solvent, the initial weight
of aqueous mixture, and the initial weight of the dry, ethanol-free
solvent.

If the feed composition is plotted on a ternary solvent, water, and
solute diagram and the equilibrium ethanol composition in the aqueous
phase is measured by GC analysis on a solvent-free basis, then the
ethanol composition in the organic phase can be determined by: (1)
projecting from the ethanol-water edge of the diagram at the point of
equilibrium concentration on a solvent-free basis toward the solvent
vertex until intersecting the mutual solubility curve on the aqueous side
and (2) projecting from the step (1) intersection through the feed
composition point until intersecting the mutual solubility curve on the
solvent side. The compositon of the organic phase is then read from the
ternary diagram at the latter point of intersection.

This method is useful for determining water distribution coefficients when the solvent tends to be wet, but it is inaccurate whenever the solvent is dry and/or the mutual solubility curve is difficult to reproduce on the solvent side. In this case, it is more accurate to chromatograph a sample of the equilibrated solvent to obtain the ethanol to water weight percentage on a solvent-free basis. The separation factor may then be easily calculated from the ethanol-to-water ratios that were obtained from the GC analysis for the aqueous and organic samples at equilibrium, but both on a solvent-free basis.

Given the initial organic and aqueous weights, the initial ethanol weight fraction, and the final ethanol weight fractions in the aqueous and organic phases on a solvent-free basis, then the solvent, ethanol and water material balances may be solved simultaneously if the weight fraction of solvent in the equilibrium aqueous phase is also known. In many cases when the ethanol concentration is low, the solvent weight fraction in the equilibrium aqueous phase is essentially zero and can be negelected. Otherwise, the solvent weight fraction in the equilibrium aqueous phase may be determined from the mutual solubility curve.

Mutual solubility curves and experimental tie lines based upon GC analysis and cloud point titrations are presented for several systems in Figs. 1 thru 22. For solvents that consist of only a single chemical species (e.g. 2-ethylhexanol) the ternary diagram represents a complete picture of the two phase equilibria. However, for the blended systems, consisting of two or more chemical species, the ternary diagram is only
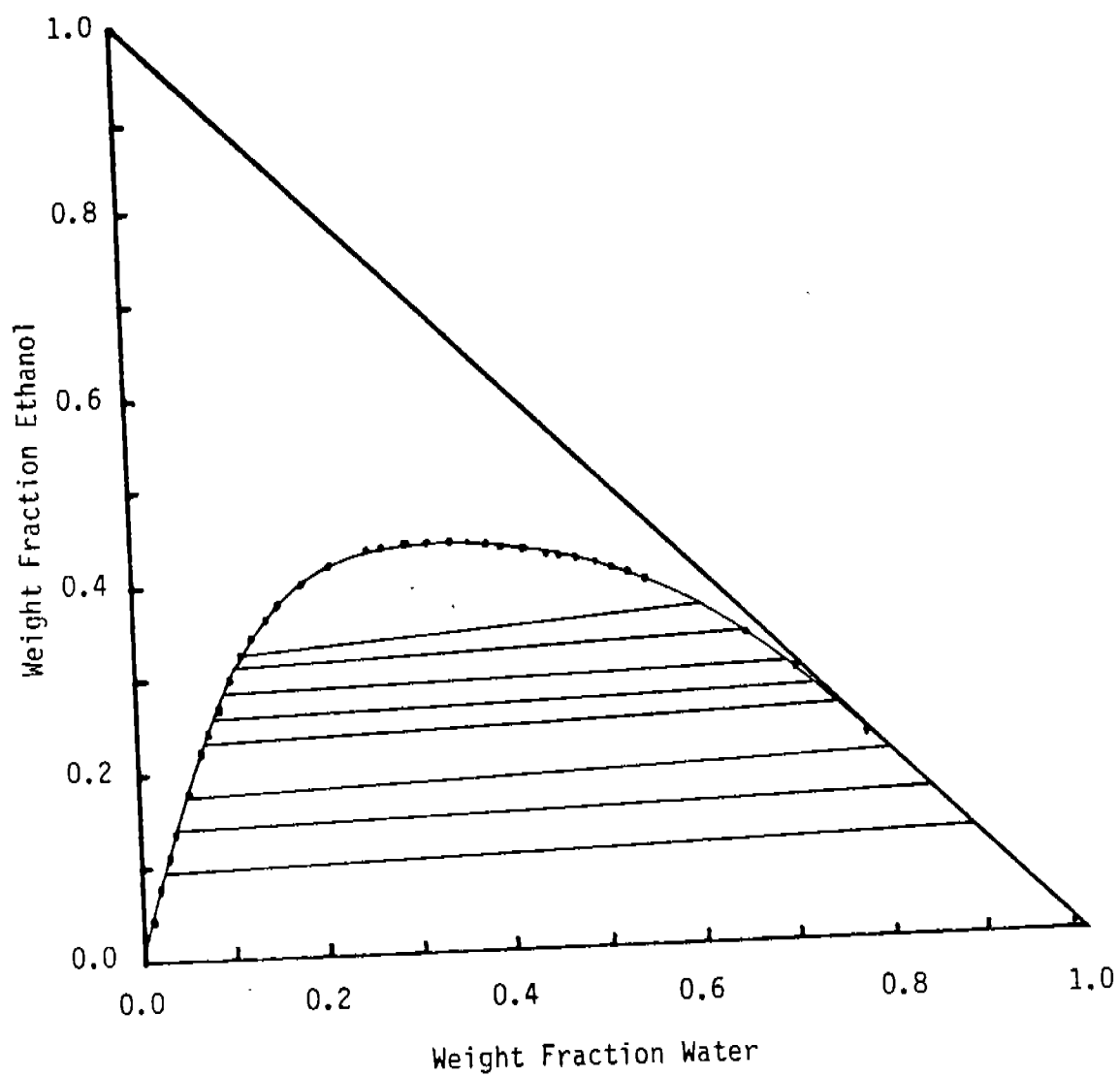
Fig. 1 Mutual solubility curve for the system: ethanol, water, and the solvent 2-ethylhexanol.
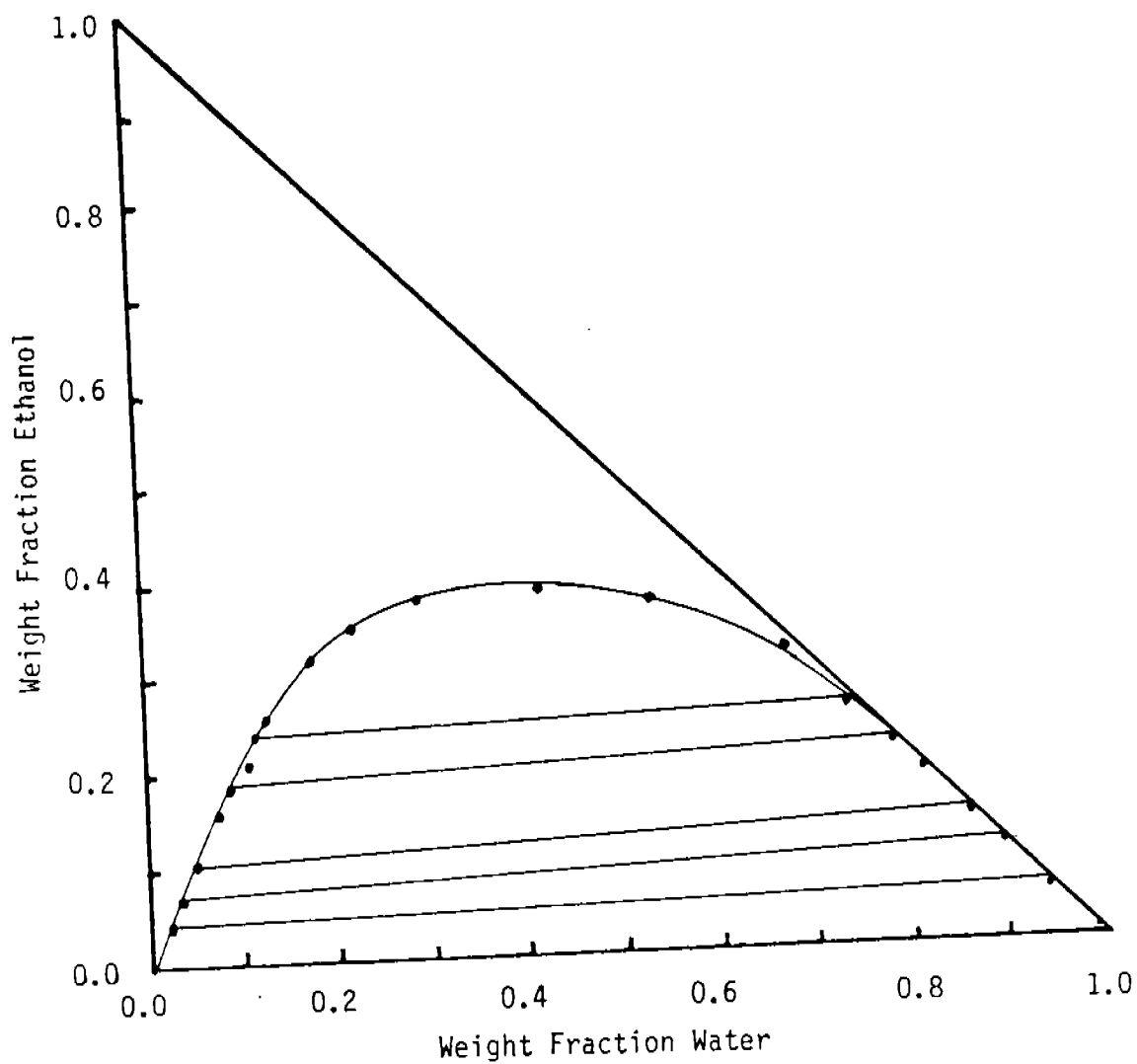
Fig. 2   Mutual solubility curve for the system: ethanol, water, and the solvent 2-octanol.
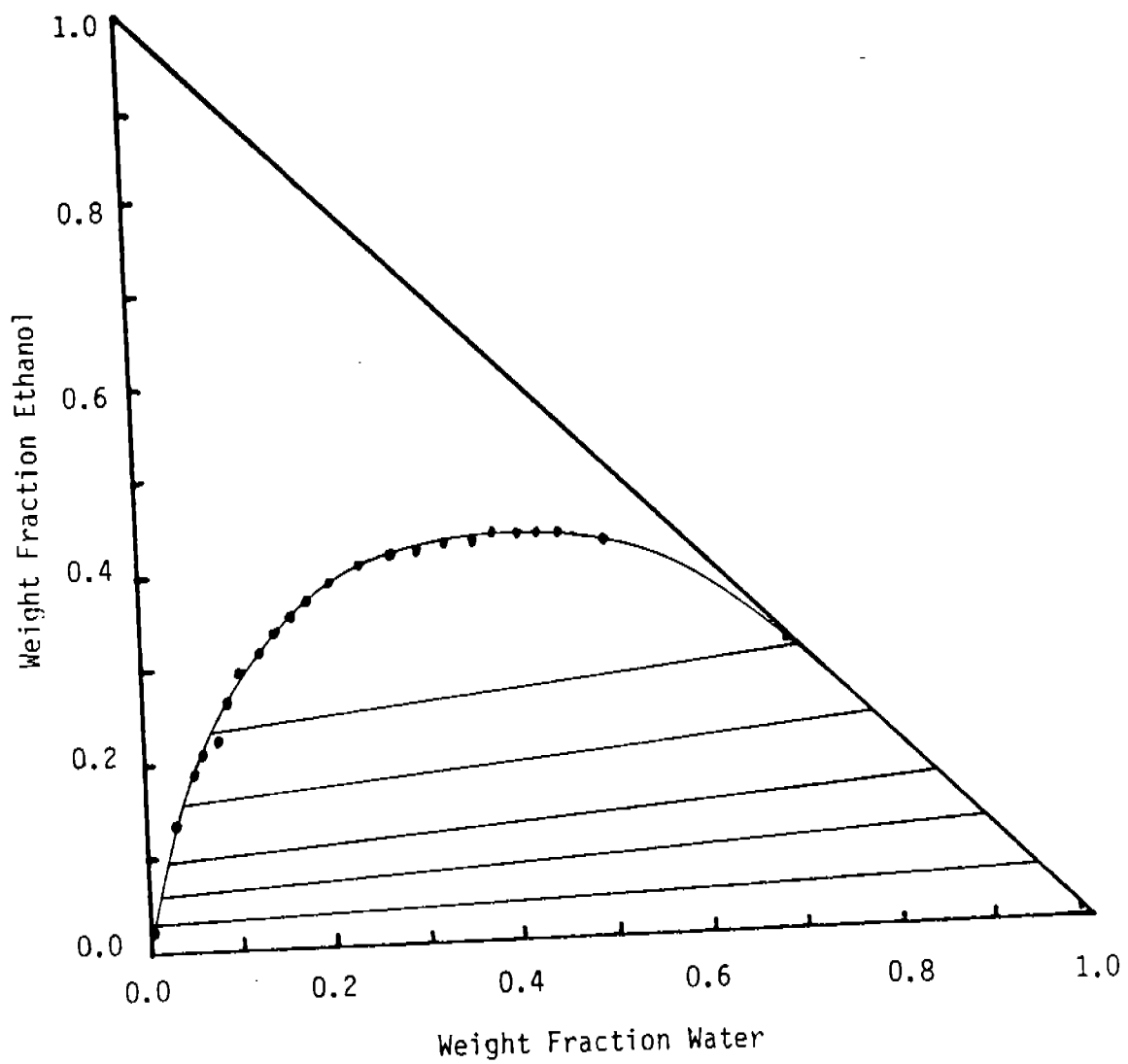
Fig. 3   Mutual solubility curve for the system: ethanol, water, and the solvent decyl alcohol.
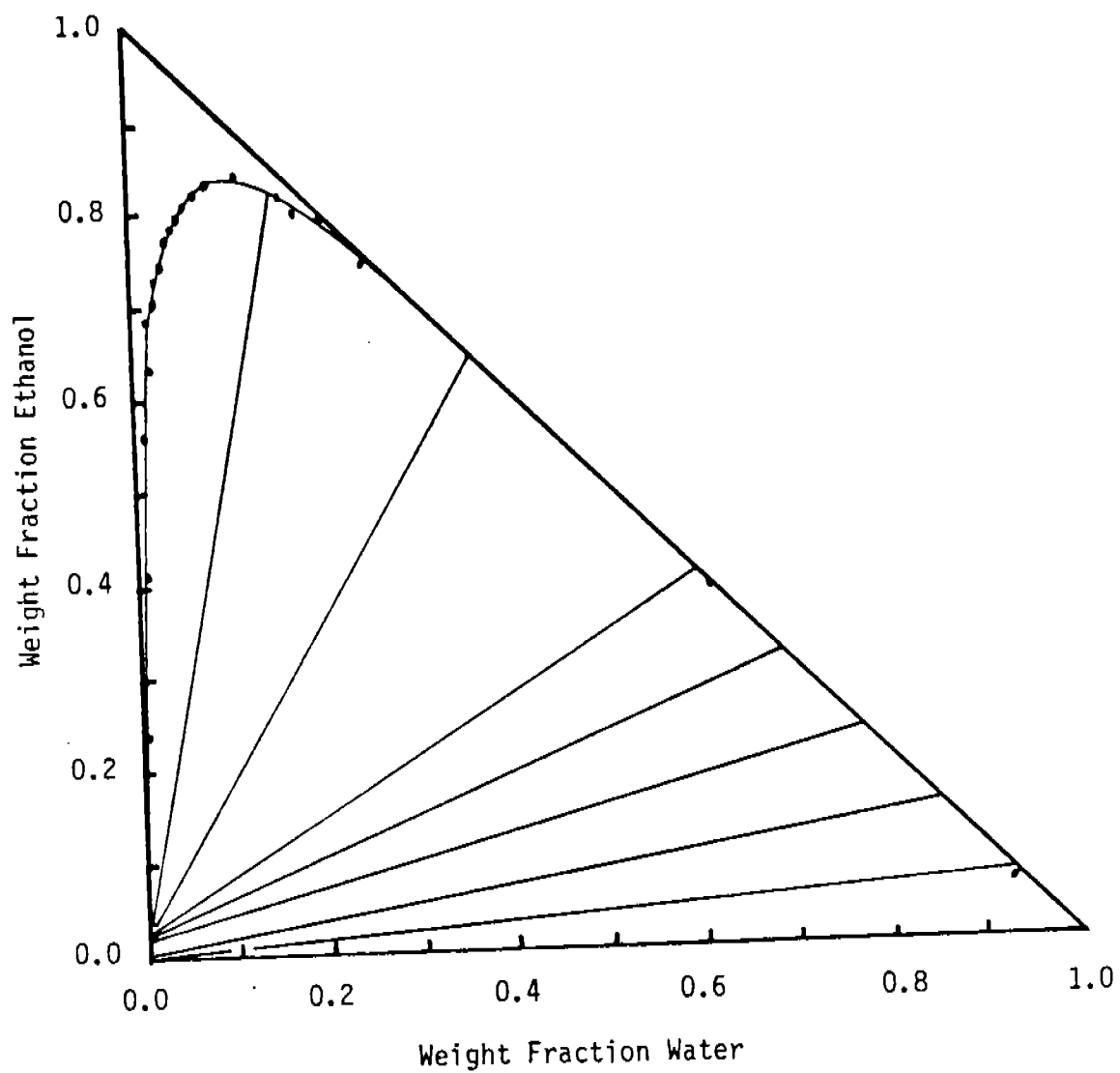
Fig. 4   Mutual solubility curve for the system: ethanol, water, and the solvent consisting of pure kerosene.
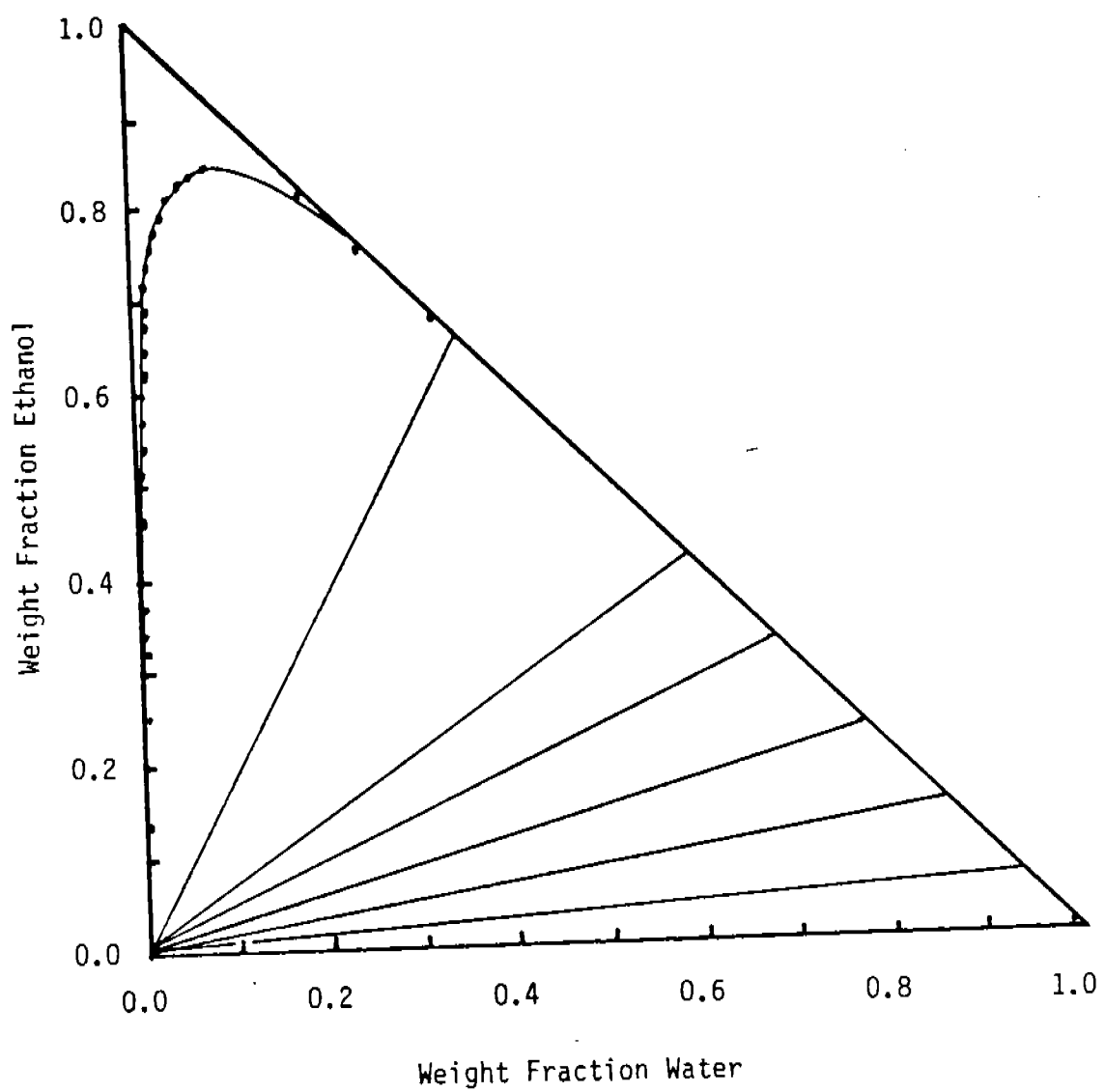
Fig. 5 Mutual solubility curve for the system: ethanol, water, and the solvent NORPAR-12.
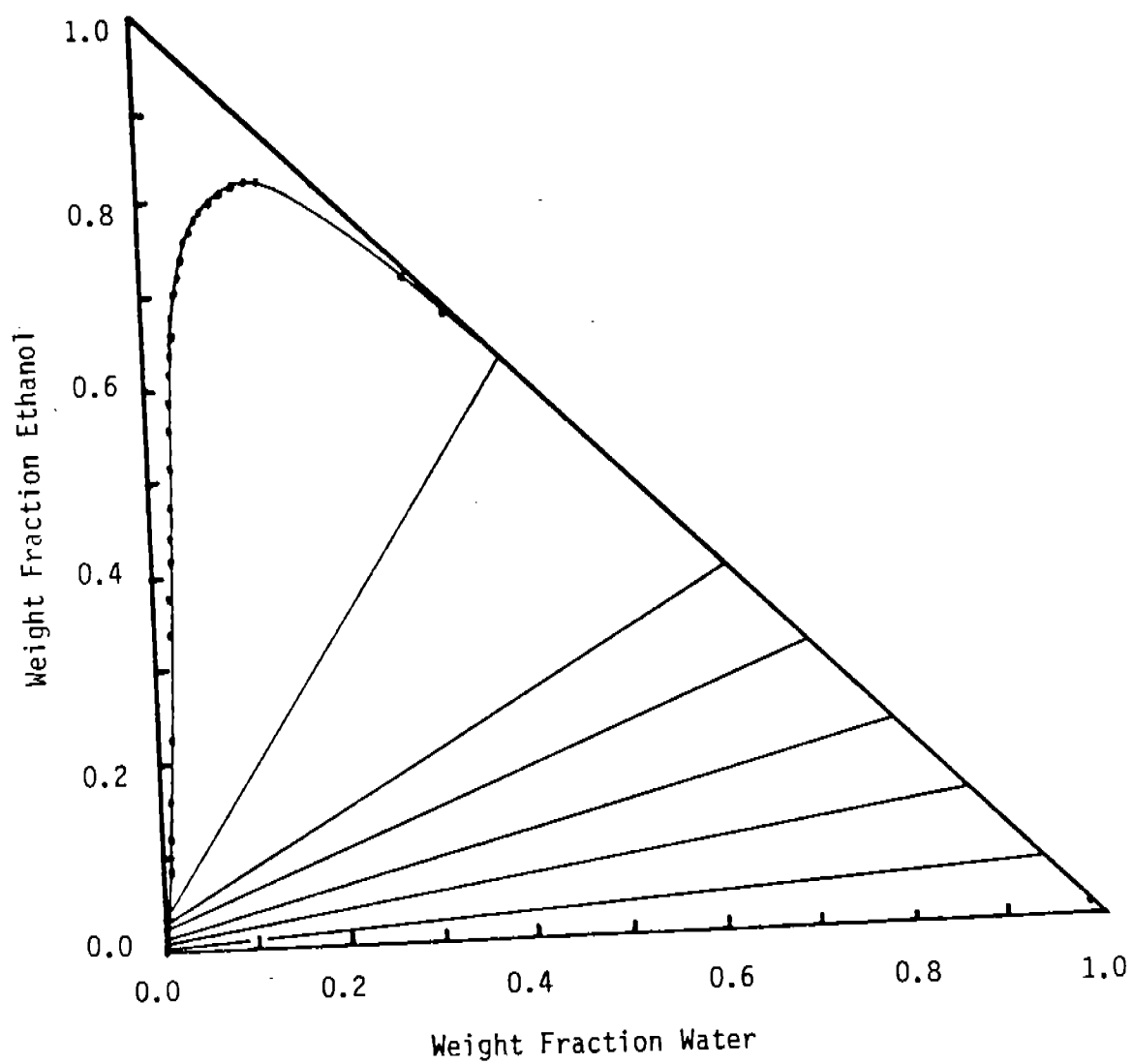
Fig. 6   Mutual solubility curve for the system: ethanol, water, and the solvent 10 vol % tridecyl alcohol in kerosene.
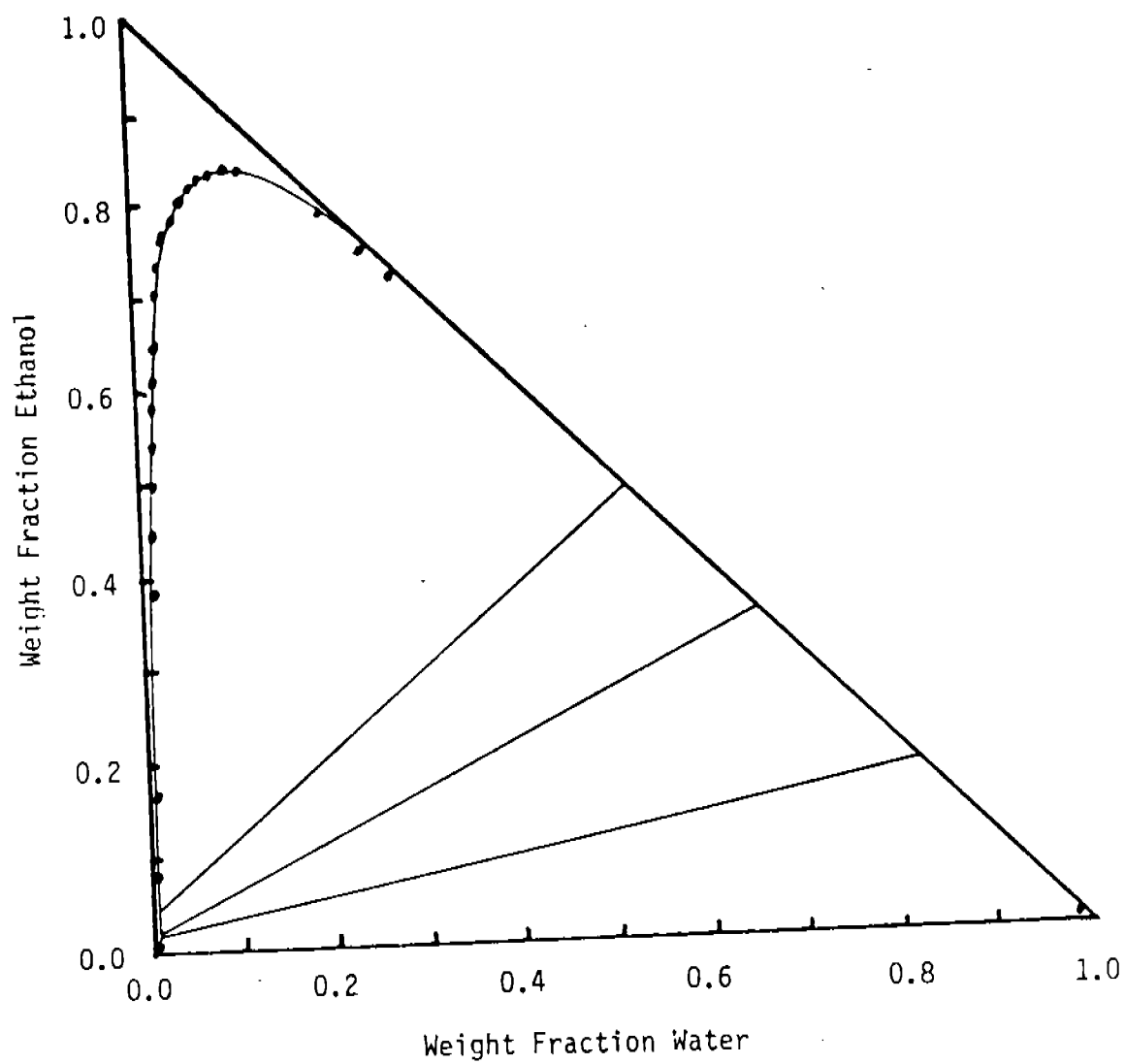
Fig. 7   Mutual solubility curve for the system: ethanol, water, and the solvent 10 vol % p-dodecyl phenol in n-dodecane.
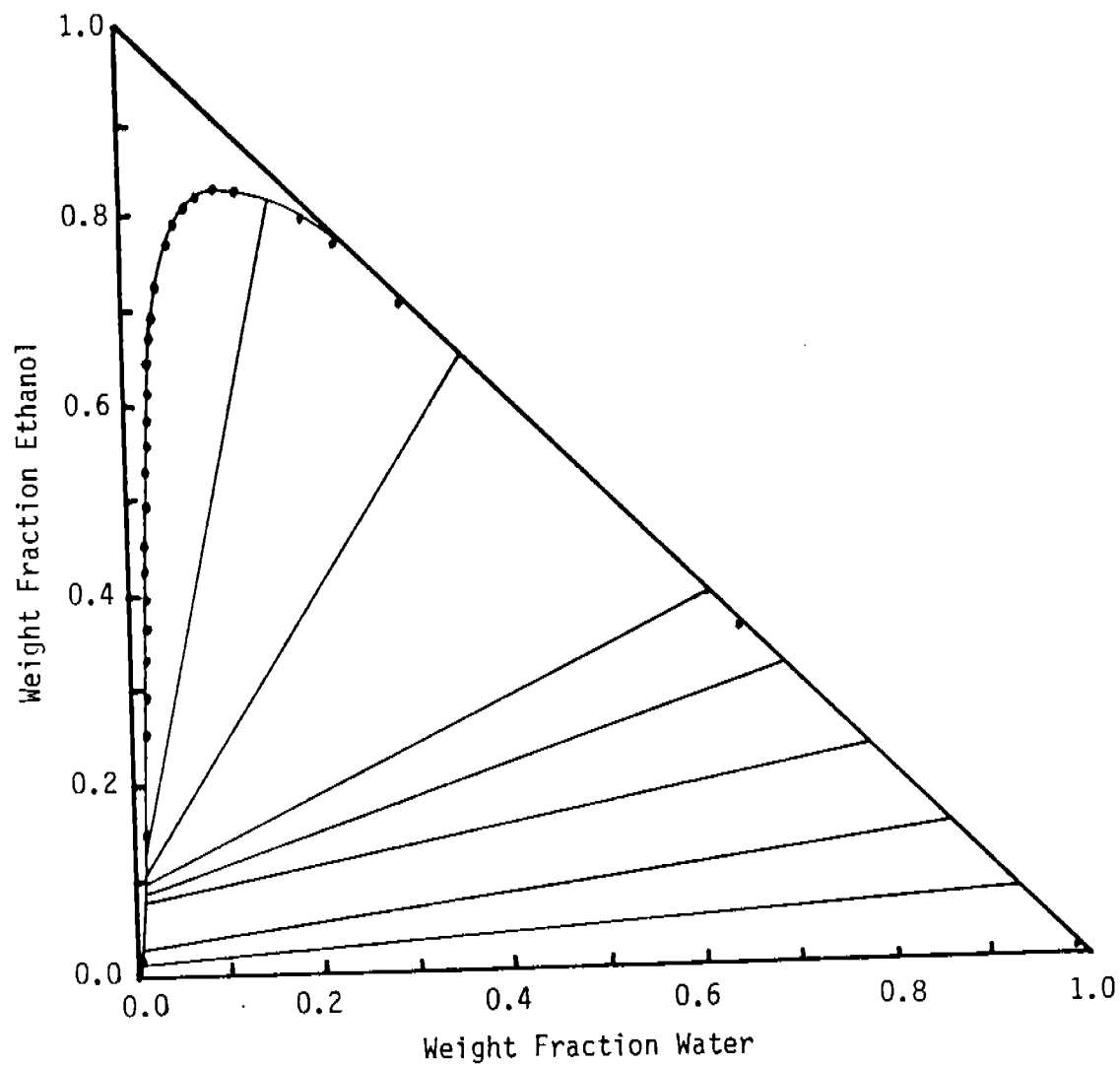
Fig. 8. Mutual solubility curve for the system: ethanol, water, and the solvent 10 vol % dodecyl alcohol in NORPAR-12.
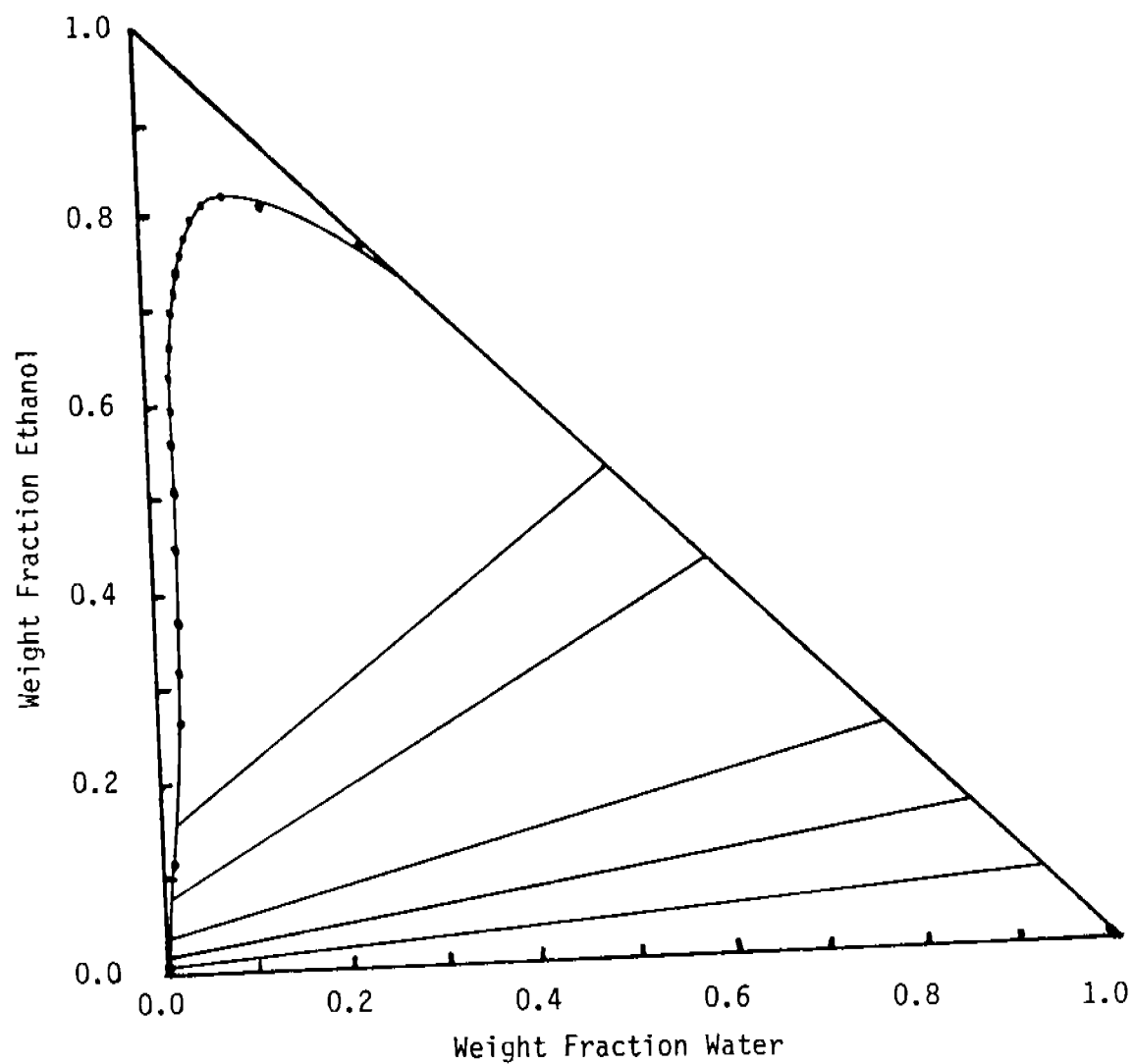
Fig. 9. Mutual solubility curve for the system: ethanol, water, and the solvent 20 vol % tridecyl alcohol in NORPAR-12.
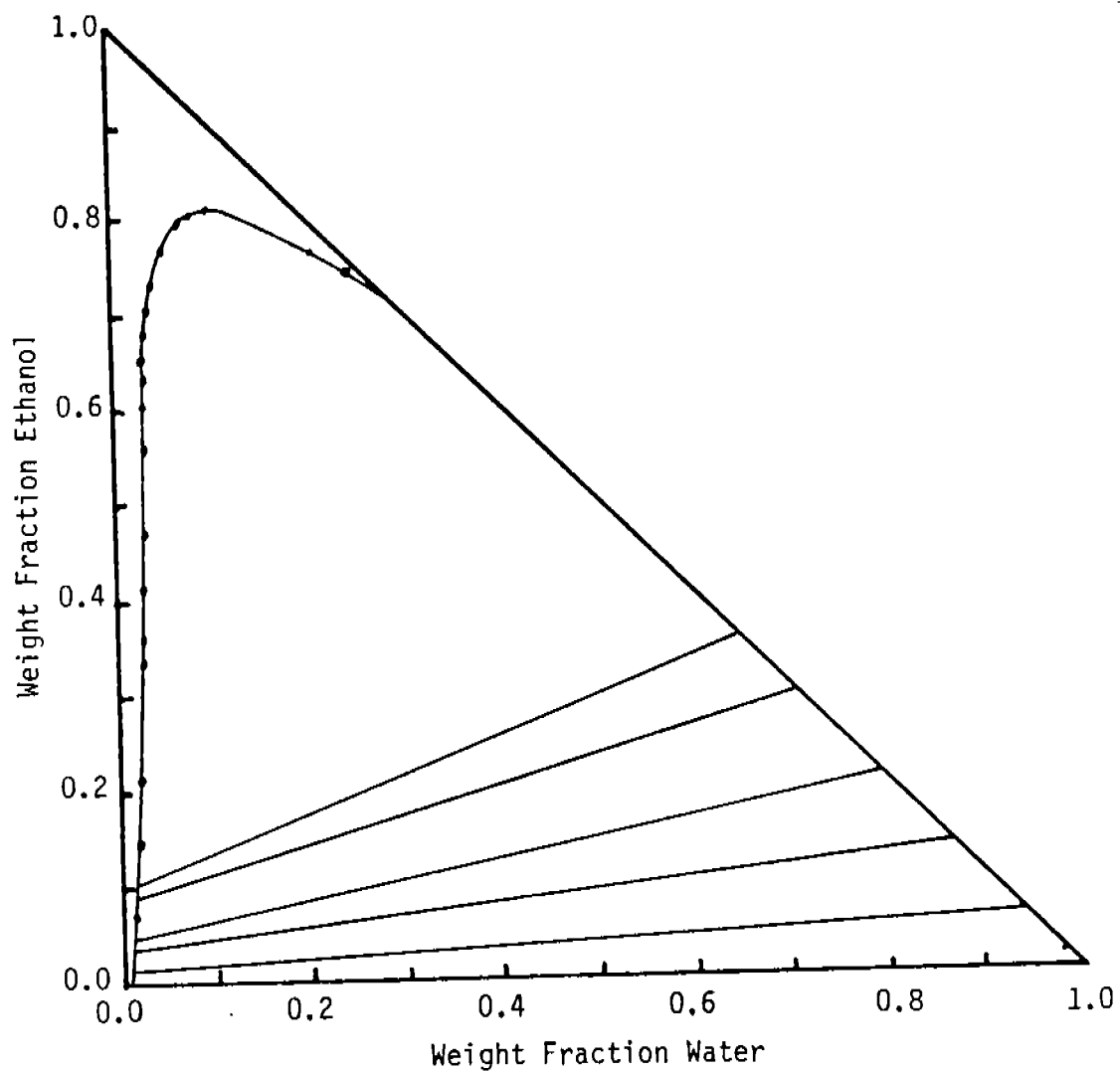
Fig. 10. Mutual solubility curve for the system: ethanol, water, and the solvent 30 vol % TBP in NORPAR-12.
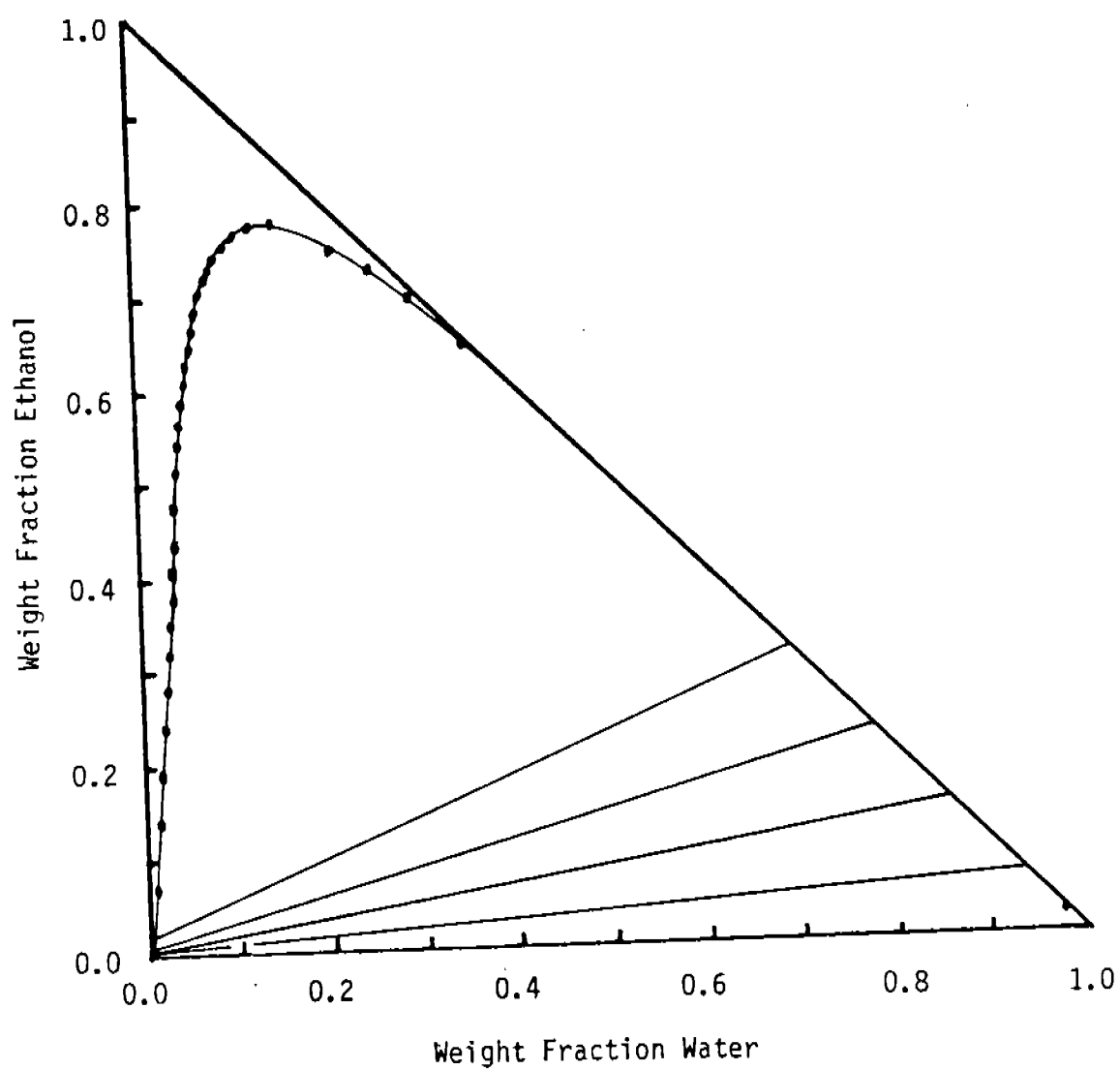
Fig. 11 Mutual solubility curve for the system: ethanol, water, and the solvent 30 vol % tricresyl phosphate in Chevron Alkylate 21.
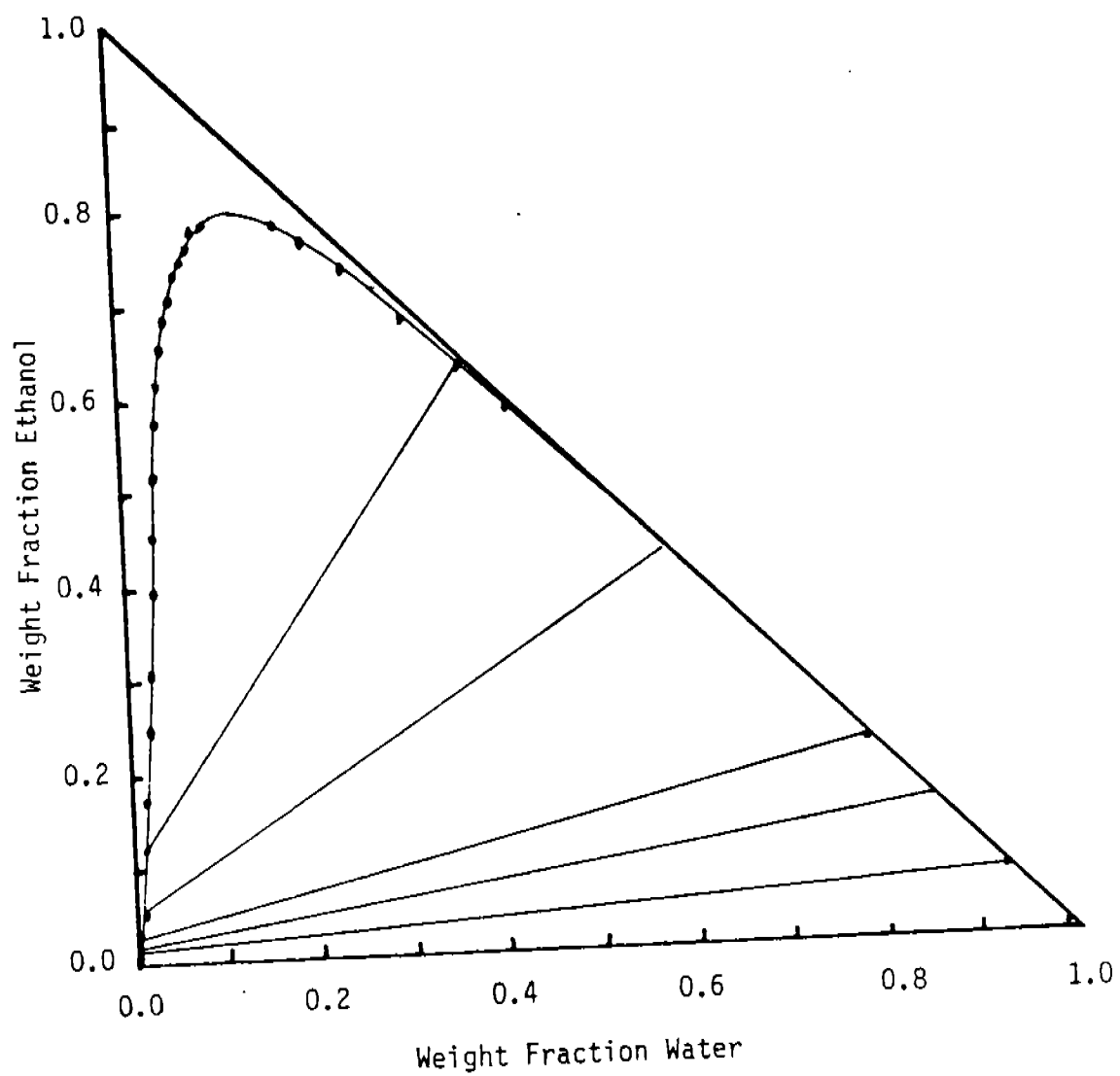
Fig. 12 Mutual solubility curve for the system: ethanol, water, and the solvent 30 vol % di-2-ethylhexyl, 2-ethylhexyl phosphonate in NORPAR-12.
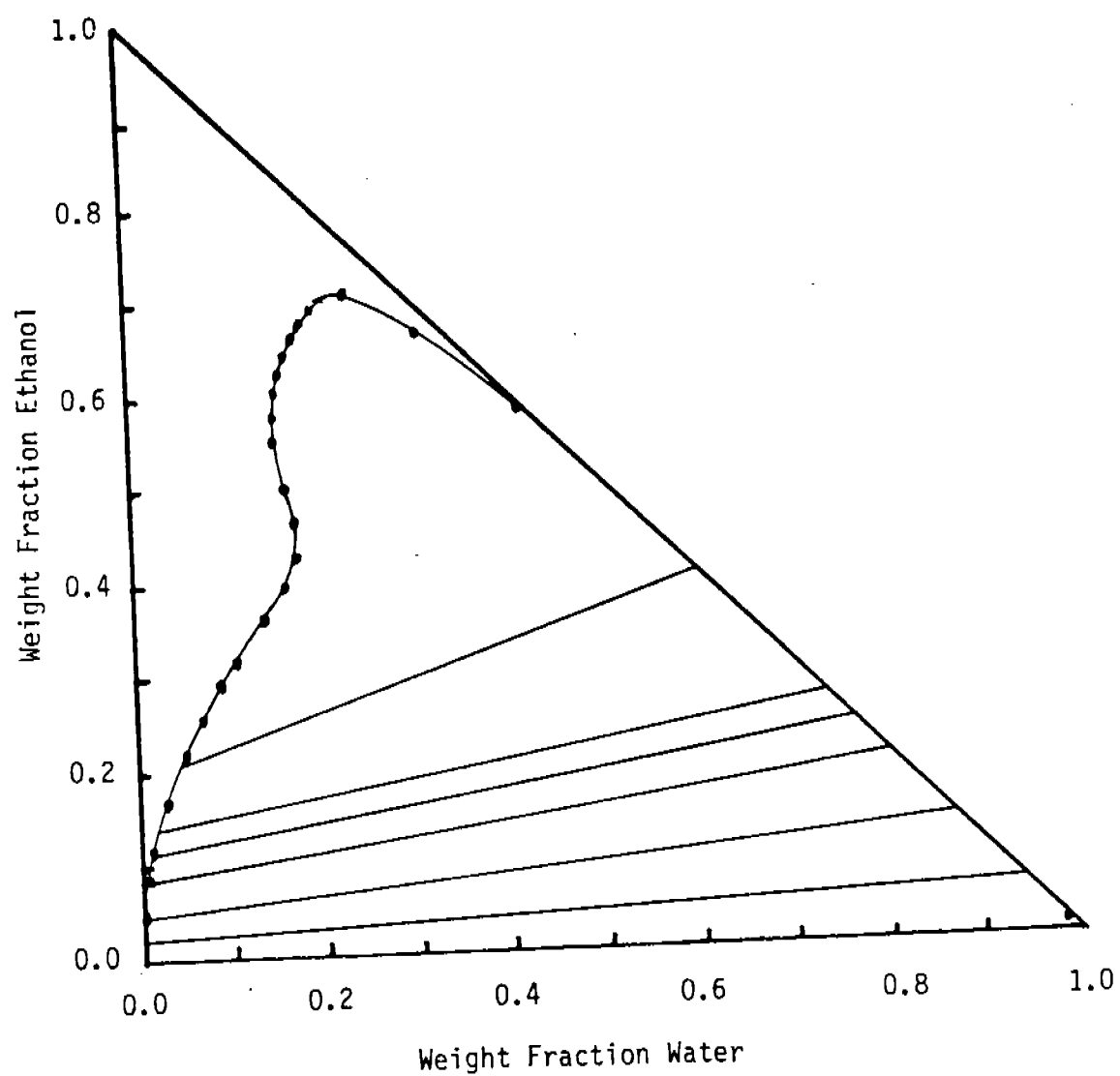
Fig. 13 Mutual solubility curve for the system: ethanol, water, and the solvent 50 vol % 2-ethylhexanol in ISOPAR-G.
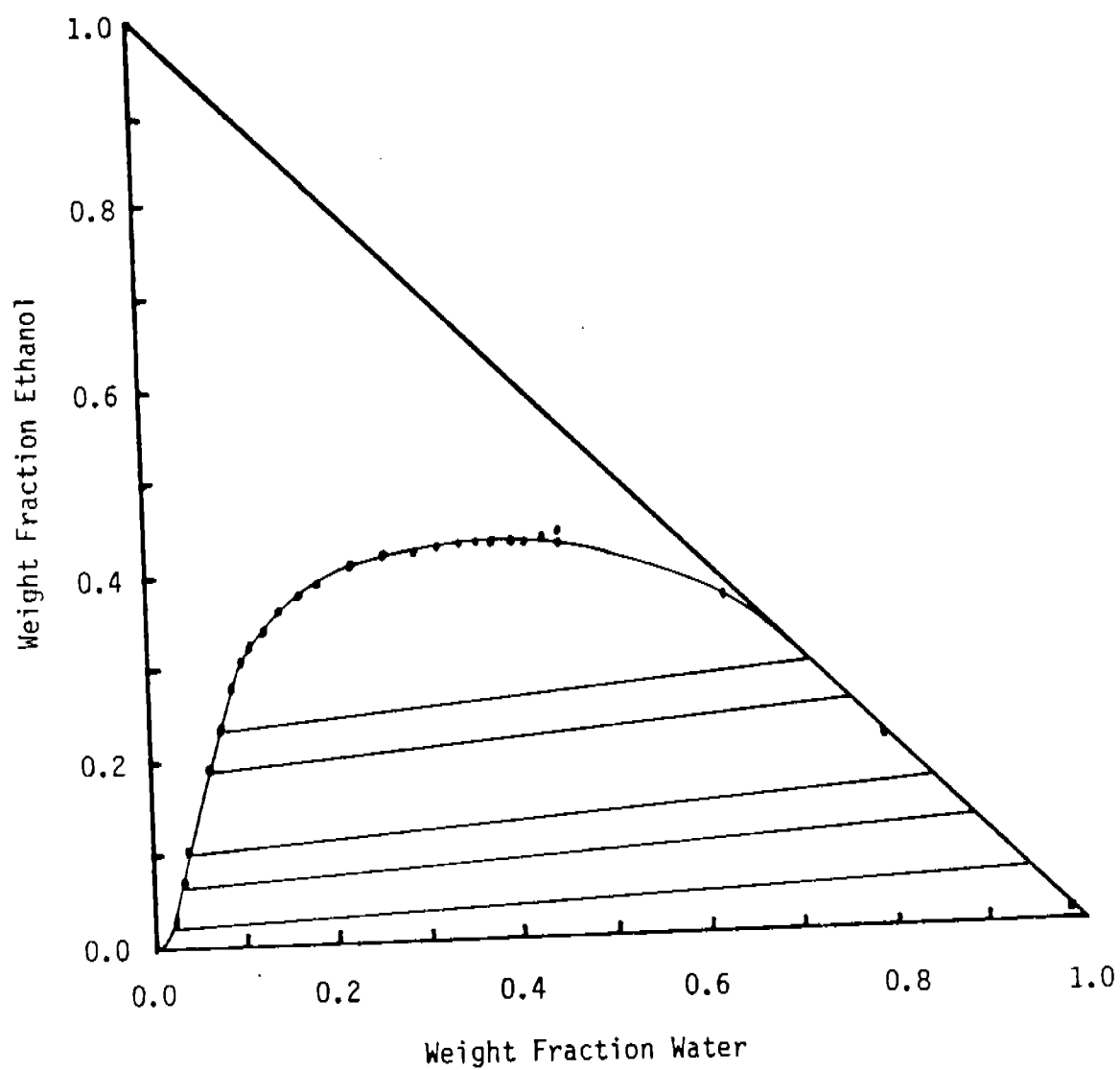
Fig. 14   Mutual solubility curve for the system: ethanol, water, and the solvent 50 vol % 2-ethylhexanol in the Conoco diol.
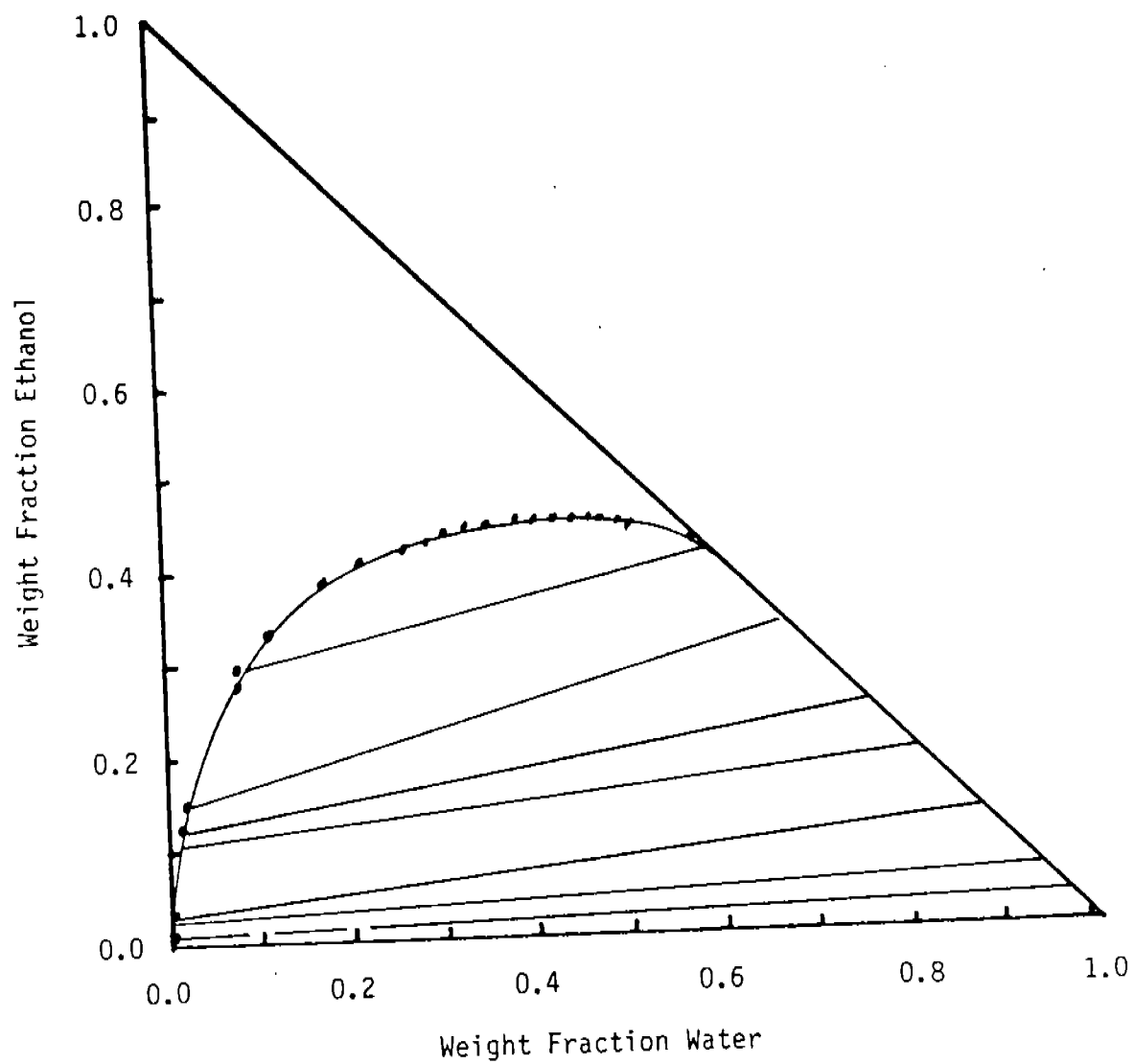
Fig. 15 Mutual solubility curve for the system: ethanol, water and the solvent 50 vol % tridecyl alcohol in tetrachloroethane.
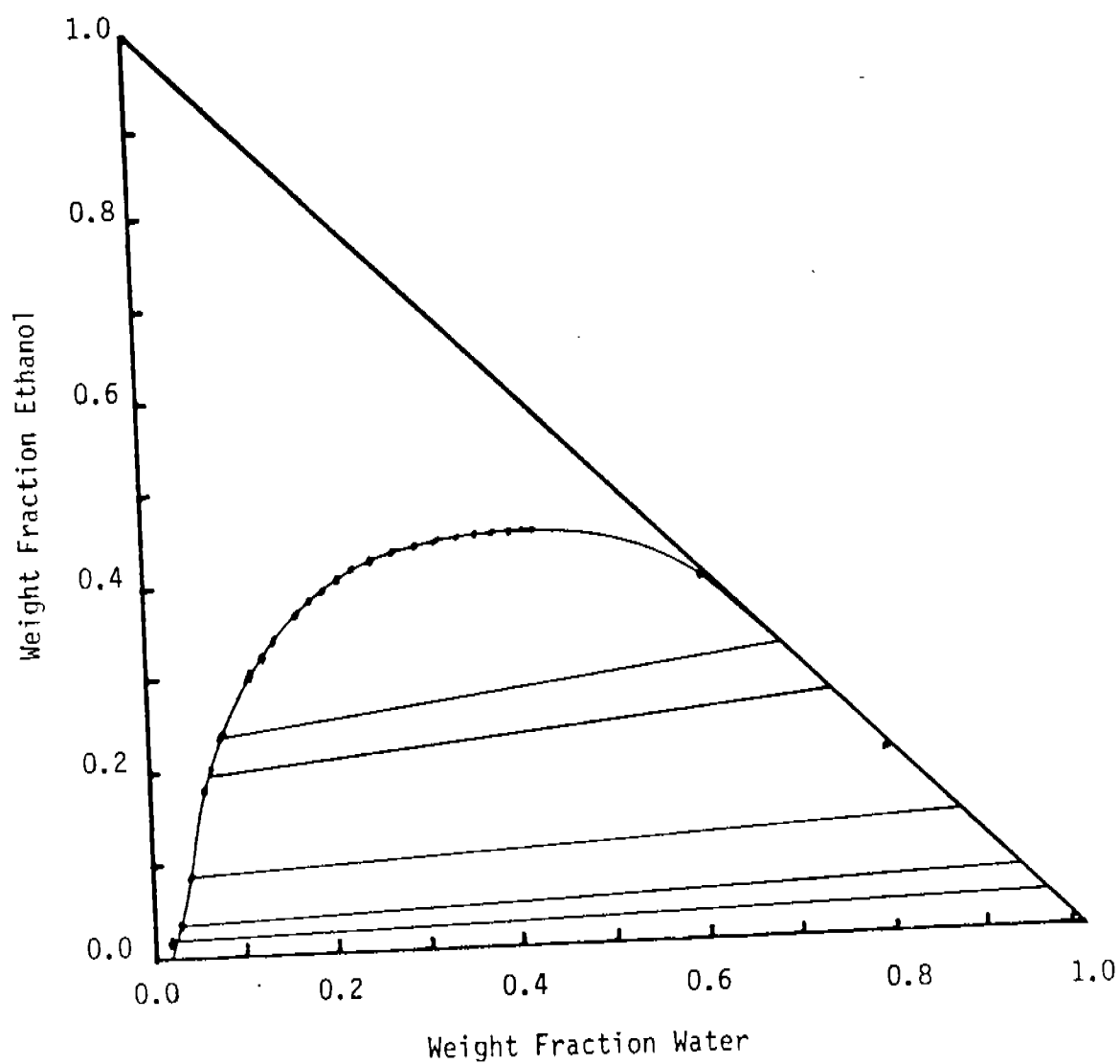
Fig. 16 Mutual solubility curve for the system: ethanol, water, and the solvent 50 vol % tridecyl alcohol in 2-ethylhexanol.
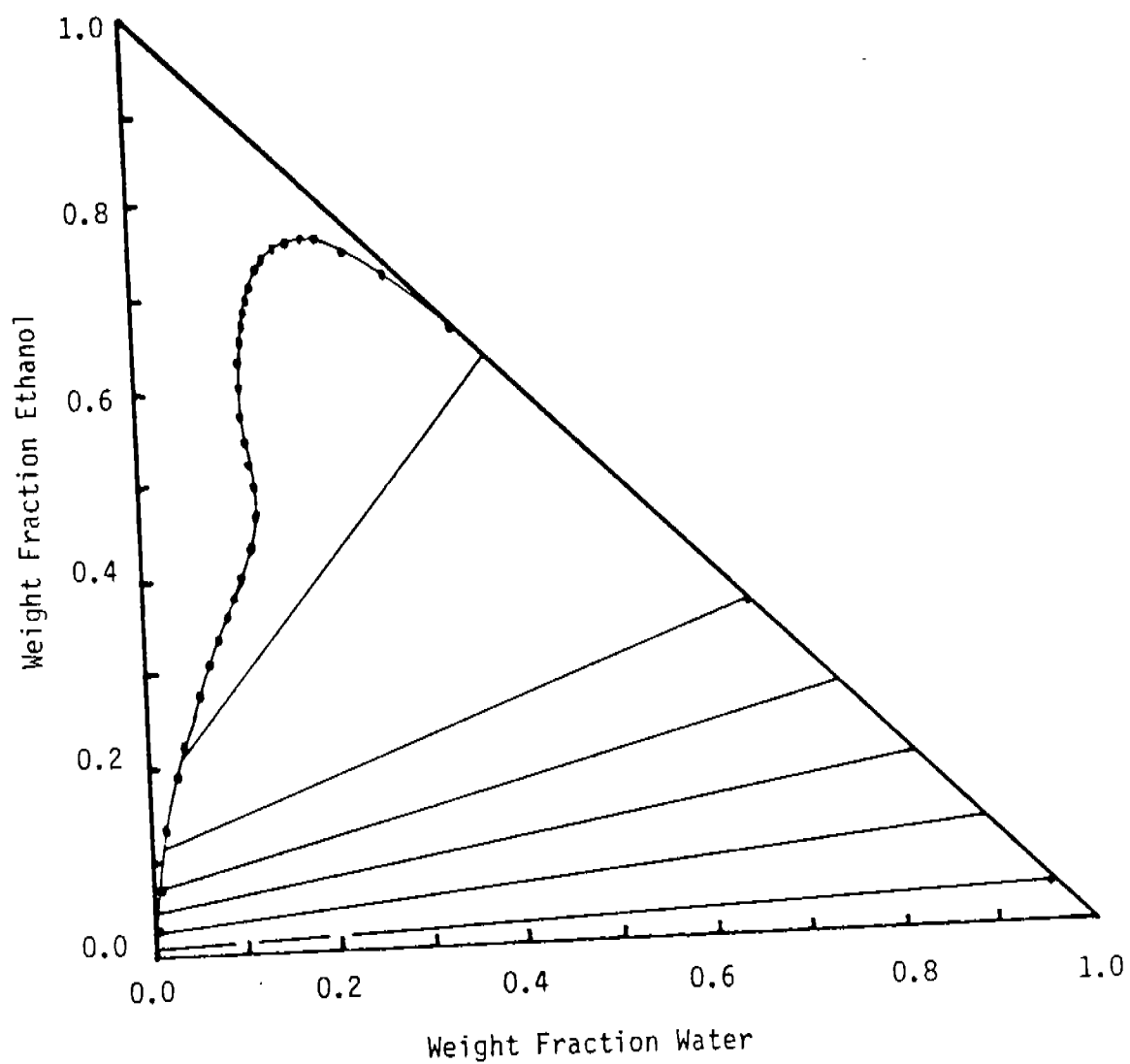
Fig. 17   Mutual solubility curve for the system: ethanol, water, and the solvent 50 vol % tridecyl alcohol in NORPAR-12.
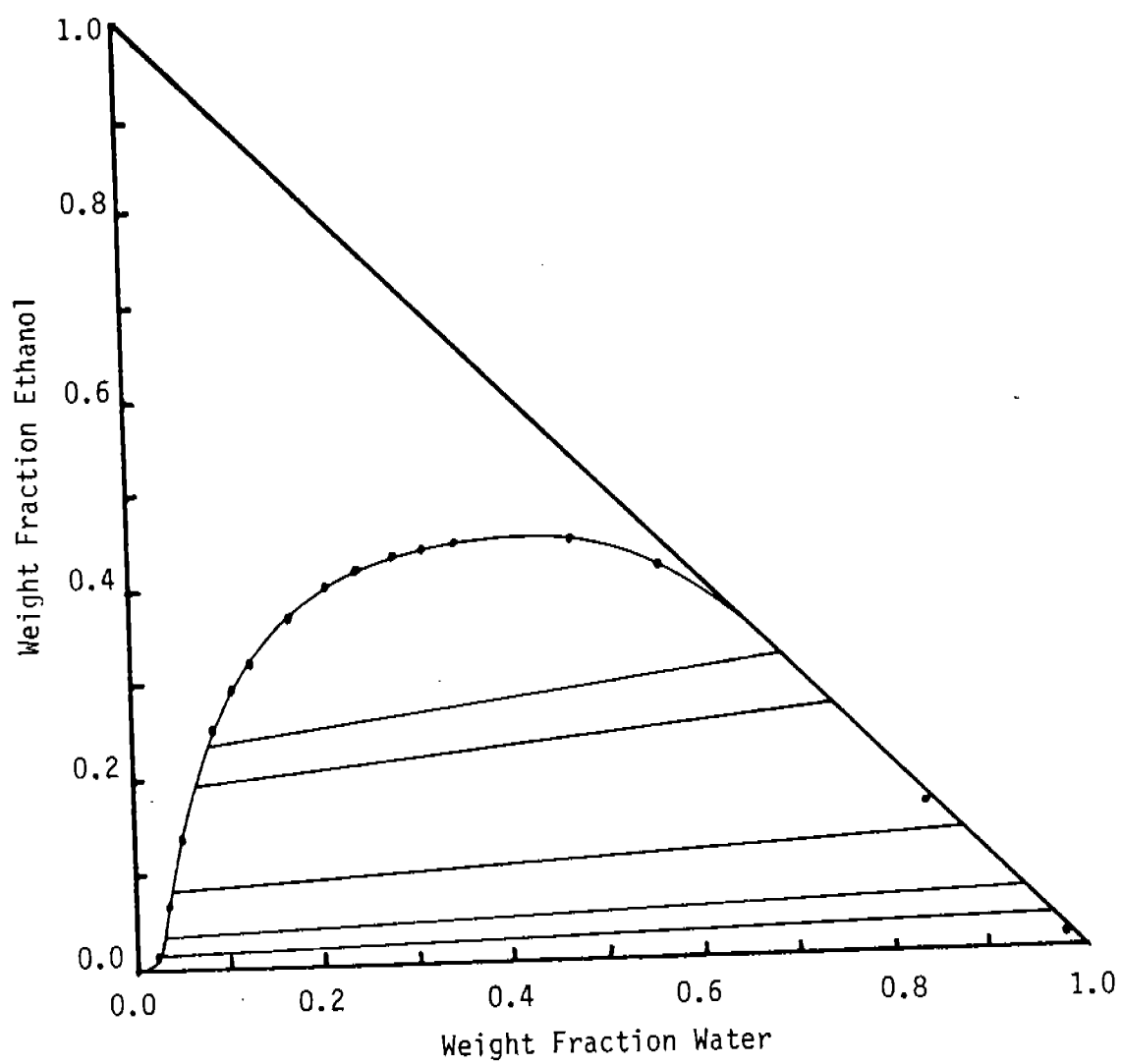
Fig. 18. Mutual solubility curve for the system: ethanol, water, and the solvent 50 vol % tridecyl alcohol in 2-ethyhexanol.
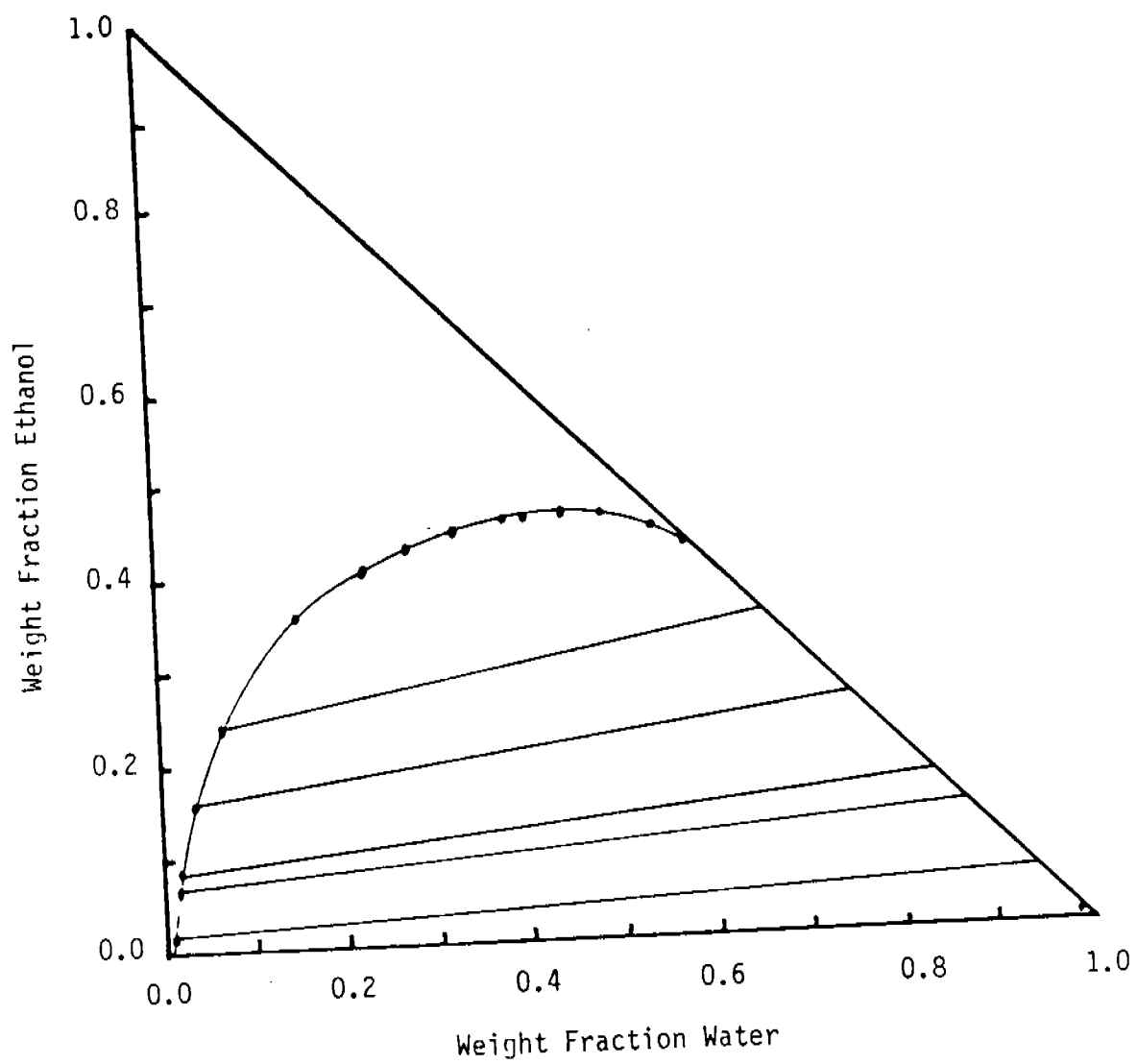
Fig. 19   Mutual solubility curve for the system: ethanol, water, and the solvent 70 vol % tridecyl alcohol in 2-ethylhexanol.
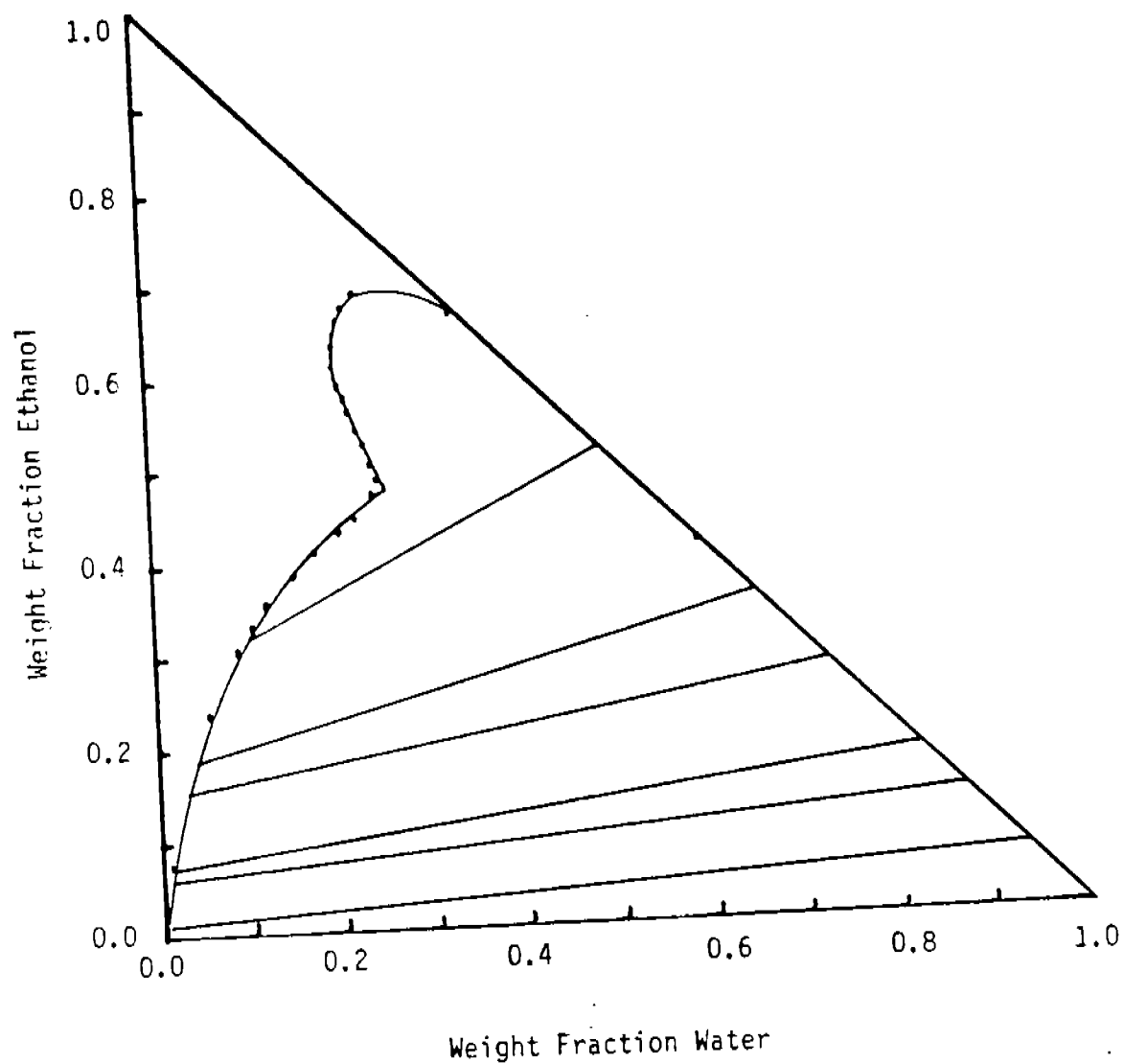
Fig. 20 Mutual solubility curve for the system: ethanol, water and the solvent 30 vol % NORPAR 12, 35 vol % 2-ethylhexanol and 35 vol % tridecyl alcohol.
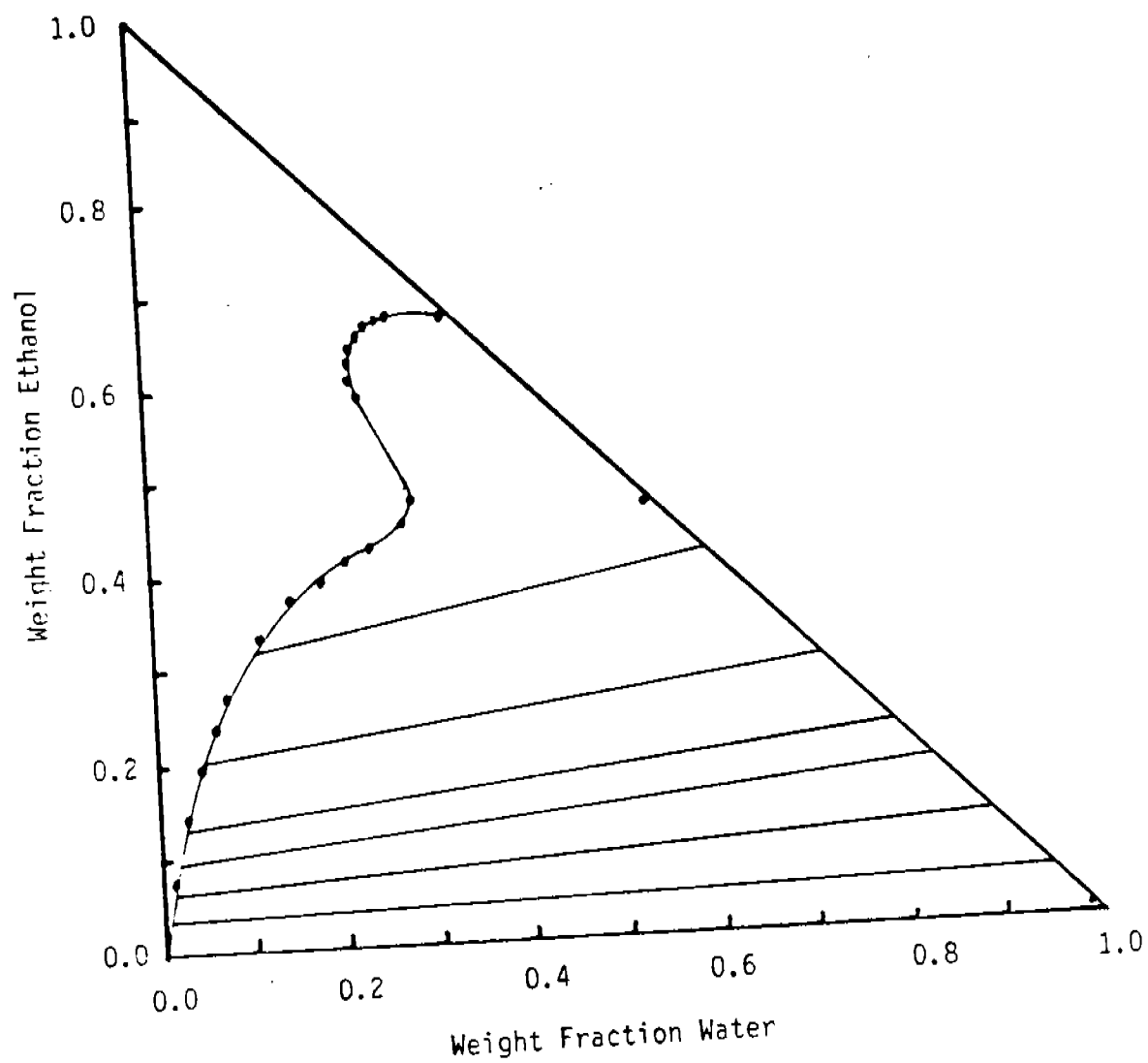
Fig. 21   Mutual solubility curve for the system: ethanol, water, and the solvent 25 vol % decyl alcohol, 50 vol % 2-ethylhexanol and 25 vol % NORPAR-12.
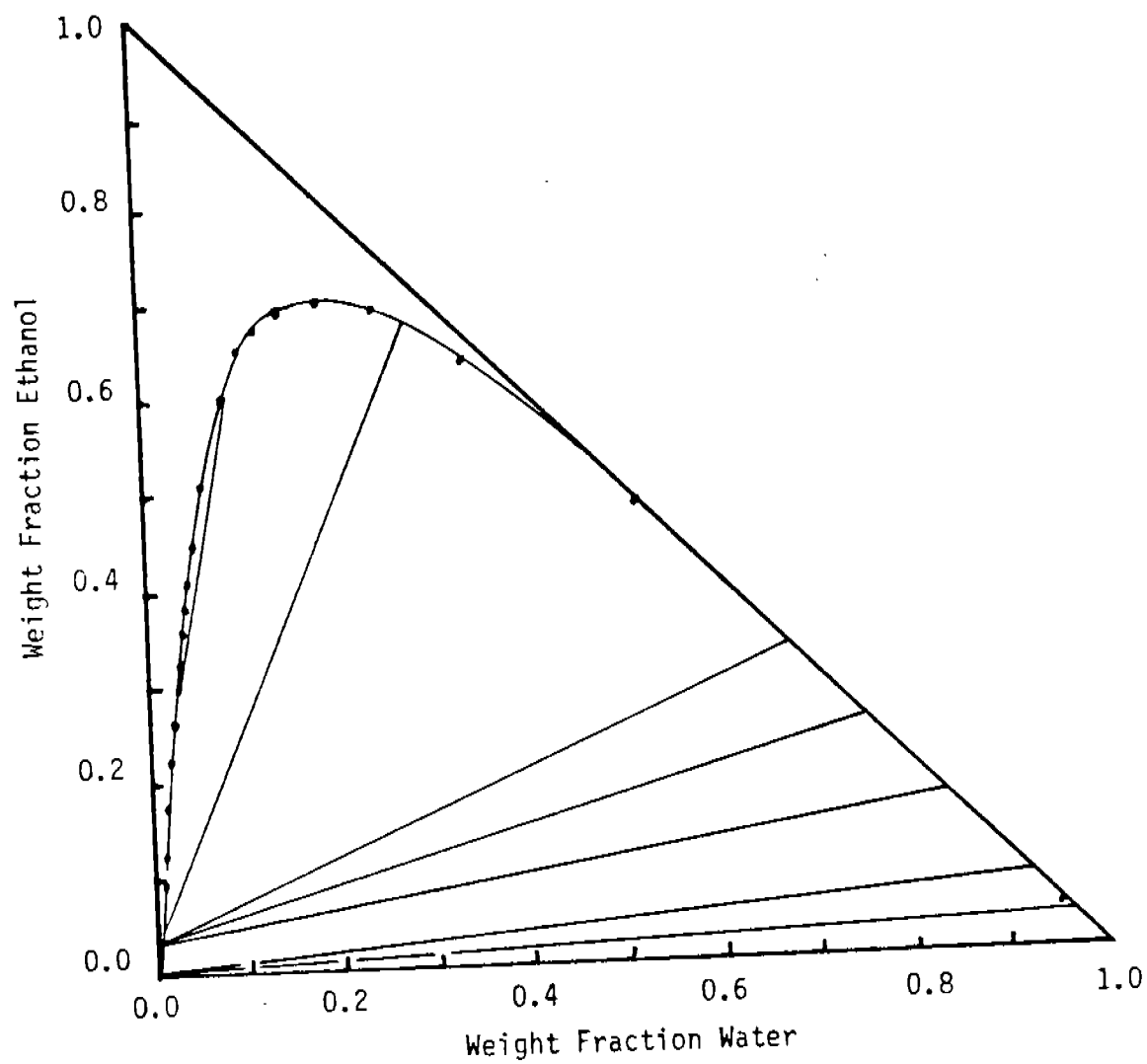
Fig. 22. Mutual solubility curve for the system: ethanol, water, and the solvent unleaded gasoline.

a partial representation. Binary solvent systems, for example, require a tetrahedral diagram to completely describe solvent behavior and the "solvent" vertex in this case simply defines one intersecting plane of the tetrahedron for the system.

All titrations and tie line determinations were performed at approximately 23 degrees Centigrade plus or minus about one degree. The shapes of the mutual solubility curves for all Type I systems that have been studied (see Figs. 1 thru 22) are such that the calculated values for the ethanol distribution coefficients are only slightly affected by inaccuracies in the mutual solubility curves. However, the water distribution coefficient calculations are more sensitive whenever the solvent system is relatively dry (e.g. 10 vol % tridecyl alcohol in NORPAR-12), but appear more accurate for the relatively wet systems (e.g. 2-ethylhexanol).

Distilled water was used to titrate the solubility curves and to make up the aqueous ethanol stock solutions for tie line determinations. The absolute ethanol came from the U.S. Industrial Chemicals Co. through the Georgia Tech Chemistry Stock Room. The GC analysis of the absolute ethanol indicated no detectable amounts of water and less than a tenth of a percent of organic impurities.

In most cases, solvents were used without additional treatment as they were received from the vendors. Some of the solvent systems were distilled before use, but high solvent purity is not always desirable. For example, the crude reaction mixture resulting from the dimerization

of 2-ethylhexanol is an oil which is soluble in diluents such as
n-dodecane. Distillation in this case converts the diol to a
crystalline solid which is insoluble in that diluent and much less
usable as an extractant. Whenever possible, the less expensive
"practical" and "technical" solvent grades were purchased. Although the
results are believed to represent the equilibrium properties of the bulk
constituents, this conclusion has not been proven. On the other hand,
the agreement with published equilibrium data is good.

2.3 Stripping Tests

Organic samples, typically about 25 milliliters, were prepared by
either equilibrating the solvent with an ethanol and water mixture or
else known weights of ethanol and water were titrated into a known
weight of solvent. In either case, the solvent phase was then placed in
a round-bottom flask with a stirring bar and stripped using the
apparatus shown in Fig. 23. Ethanol and water vapors in this system are
subjected to heat from a constant temperature bath and vacuum which
causes the vapors to migrate to the cold traps which were cooled using
liquid nitrogen.

The constant temperature bath was brought to the desired
temperature and the sample flask cut into place and allowed to
equilibrate while the connecting stopcock to the vacuum supply was
closed. After adjusting the air bleed on the vacuum supply in order to

Figure 23

VACUUM STRIPPING APPARATUS
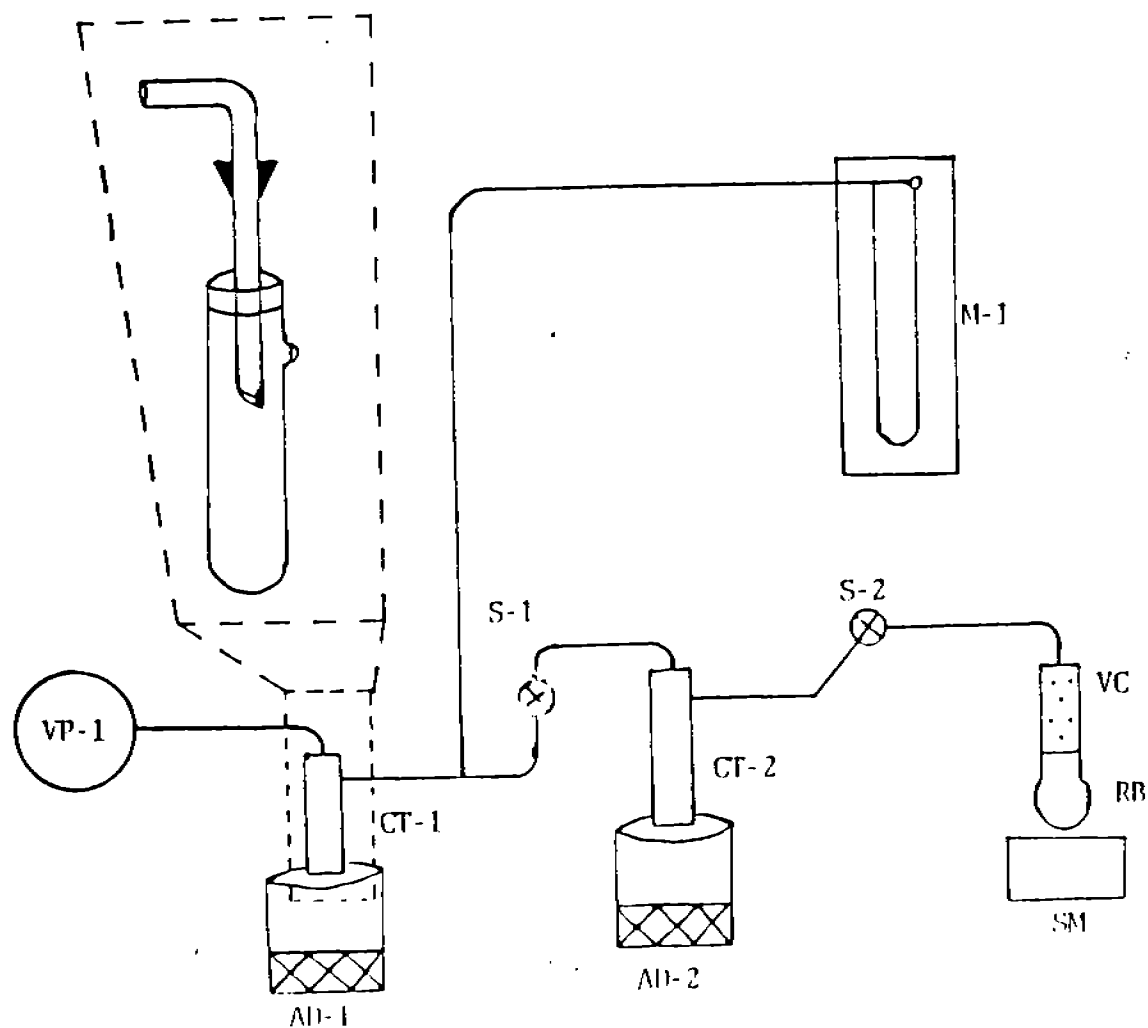
KEY

VP	VACUUM PUMP
CT	COLD TRAP
AD	ACETONE-DRY ICE BATH
SM	STIRRING MOTOR
RB	ROUND BOTTOM FLASK
VC	VIGOREAUX COLUMN
S	STOPCOCK
M	U-TUBE MONOMETER

produce the desired pressures, the glassware and tubing were warmed slightly with a heat gun to prevent any vapor condensation before the ethanol and water mixture reached the collection trap.

Next, the stopcock between the flask and the vacuum supply was opened and a timer started. Upon reaching the end of predetermined time periods, the traps were removed from the system and replaced with fresh traps in order to cut the condensed product into fractions.

In some cases, the objective of the experiment was to measure the rate at which ethanol and water were separated from the solvent by the stripping apparatus. Material balance calculations were then carried out by: (1) knowing the precise composition and initial weight of the extract (which was usually titrated), (2) measuring the weights and compositions of the product fractions and (3) measuring the final weight and composition of the stripped solvent.

When the stripping apparatus was used simply to verify a tie-line, then material balance calculations were not required. In this case, the required analysis consisted of: (1) measuring the initial and final composition of the aqueous phase before and after equilibration, (2) measuring the initial weights of organic and aqueous phases before equilibration, (3) measuring by GC analysis the organic ethanol-to-water weight ratio before stripping, (4) measuring by GC analysis the organic ethanol-to-water weight ratio after stripping and (5) measuring the composition of the condensed ethanol and water product by GC analysis. The final weight of condensate is not required in this case although it

does permit a calculation of the material unaccounted for (MUF) in the experiment.

Solvent stripping is usually accompanied by a vigorous boiling and frothing of the solvent phase while mass transfer is underway. In order to estimate equilibrium conditions at a given temperature and pressure, the test was continued usually about 30 minutes beyond that time at which bubbles ceased to appear in the solvent. The results shown in Table 4, for example, were obtained after stripping the solvent for about two hours. During the last hour, so little ethanol was recovered that the system was clearly at equilibrium. These results suggest that stripper pressures less than 10 mm Hg are required in order to obtain an adequate product recovery.

The results of two additional stripping tests are summarized in Tables 5 and 6. They suggest that most of the ethanol was stripped from the solvent solution within the first 20 minutes of the experiments. The operating pressure of about 2 mm Hg appears adequate to obtain a high product recovery from this solvent system although the initial solvent loading was somewhat higher than can be attained by equilibration.

Attempts to reproduce tie-line analysis by recovering small amounts of product were successful, but were hindered by apparent contamination problems. In particular, it was necessary to purge moisture from the stripping apparatus by boiling the solvent sample several minutes before placing the traps in liquid nitrogen. In this way, excess water was

Table 4. Stripping characteristics of 30 vol% TBP in n-dodecane.

Temperature (°C)	Pressure (mm Hg)	%Ethanol Stripped[a] at Equilibrium
35	20	58
35	10	80
50	20	84
50	10	89[b]

[a]The initial feed was 4.66 wt% ethanol, 0.16 wt% water, and 95.18 wt% 30 vol% tri-n-butyl phosphate in n-dodecane.

[b]The rapid effervescence of ethanol and water resulted in some losses. This value is a projection based upon a 9% loss.

Table 5. Stripping characteristics of 10 vol% isodecanol in n-dodecane.

	Fractions[a]			
	1	2	3	4
Cumulative Stripping Time (min)	4.9	15.6	46.8	73.5
Temperature (°C)	54	57	55	66
Pressure (mm Hg)	2.2	2.4	2.3	2.3
Weight of Recovered Fraction (gm)	13.0103	4.0888	0.0	0.0
Cumulative[b] % Recovered	75.5	99.2	99.2	99.2

[a] The initial feed was 36.9174 gm of solvent, 16.8201 gm of ethanol and 0.5209 gm of water.

[b] A maximum of 17.341 gm of ethanol and water could be recovered.

Table 6. Stripping characteristics of 10 vol% isodecanol in n-dodecane at 40 °C

| | Fractions[a] | | | |
	1	2	3	4
Cumlative Stripping Time (min)	5	20	50	80
Temperature (°C)	40	40	40	40
Pressure (mm Hg)	2.2	2.2	2.2	2.2
Weight of REcovered Fraction (gm)	13.4229	3.3089	0.0	0.0
Cumulative[b] % Recovered	80.0	99.7	99.7	99.7

[a]The initial feed was 35.887 gm of solvent, 16.3507 gm of ethanol, and 0.506 gm of water.

[b]A maximum of 16.8567 gm of ethanol and water could be recovered.

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removed from the system by the product vapors. On the other hand, if air was inadvertently allowed to bleed through the trap, then water condensate rapidly collected even though the air was passed through a drying tube before entering the trap. Considering the humidity in Atlanta, this result is not surprising and it emphasizes the importance of providing adequate ethanol product protection from moisture.

2.4 Extractant Synthesis

In order to develop a selective extractant for ethanol recovery from dilute aqueous solutions, a series of organic molecule have been synthesized. These include a wide variety of functionalities with varying degrees of hydrophilic-lipophilic characteristics. The organic extractants have been constructed in such a way that ethanol complexation is enhanced while the interaction of the extracting agent with water has been diminished or (ideally) completely eliminated. It has been recognized that zwitter-ionic structures (or semi-polar bonds) in which the negative charge protrudes into the solvent and the positive charge is immersed in a hydrophobic environment are important structural features. It has also been recognized that hydroxyl functionalities and groups of hydroxyl functionalities are effective hydrogen bonding agents for ethanol. Coupling these molecular features with a hydrocarbon framework which is hydrophobic enough to remain in the organic layer and to diminish interaction (complexation) with water molecules should result in a more effective extraction system.

The following is a list of symmetric and unsymmetric alkyl and aryl phosphates, phosphine oxides, sulfoxides, sulfones, amine oxides and quaternary ammonium and phosphonium salts which have been synthesized for extraction investigations. The approaches which were used to synthesize each of these structures are summarized in the following section.

Symmetric and unsymmetric trialkyl and triaryl phosphates have been prepared from the reaction of the corresponding organic alcohols with phosphorous oxychloride in pyridine (Reactions 1, 2, and 3) (see Refs 12-15).

$$3 \; CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-}OH \; + \; POCl_3 \; \xrightarrow{\;N\;} \; (CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_2\text{-}O\,)_3\,P\text{-}O \qquad (1)$$

Trineopentyl phosphate

$$2 \; CH_3\text{-}C\text{-}OH \; + \; POCl_3 \; \xrightarrow{\;N\;} \; \left(CH_3\right)_3\!C\text{-}O\,)_2\,P\text{-}Cl \; \xrightarrow{\quad} \qquad (2)$$

di-t-butyl-cyclohexyl phosphate

$$+ \; POCl_3 \; \xrightarrow{\;N\;} \qquad (3)$$
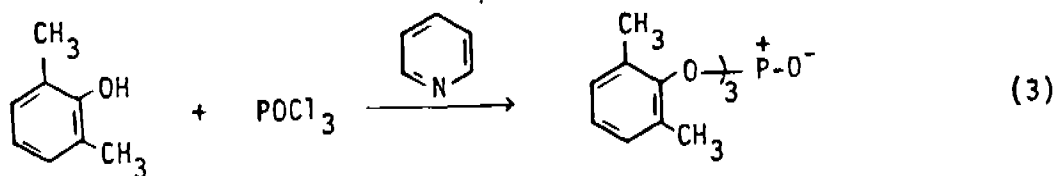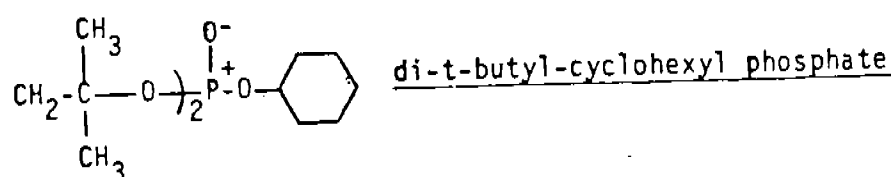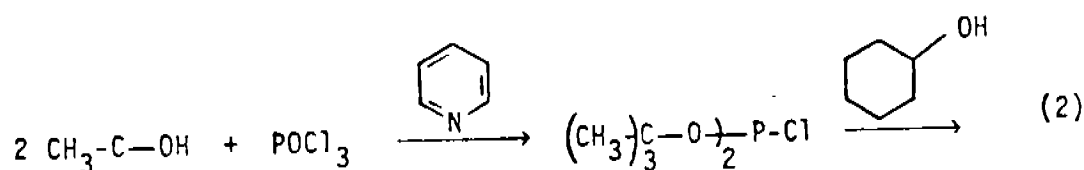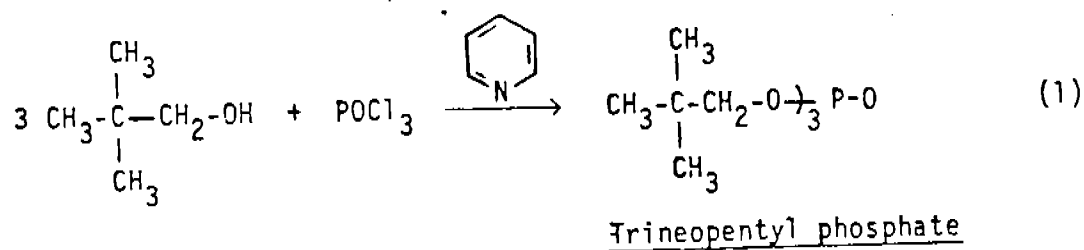
Triarylphosphine oxides have been prepared from the triarylphosphine precursor and m-chloroperbenzoic acid (Reaction 4, also see ref. 15).

Triphenylphosphine oxide

(4)
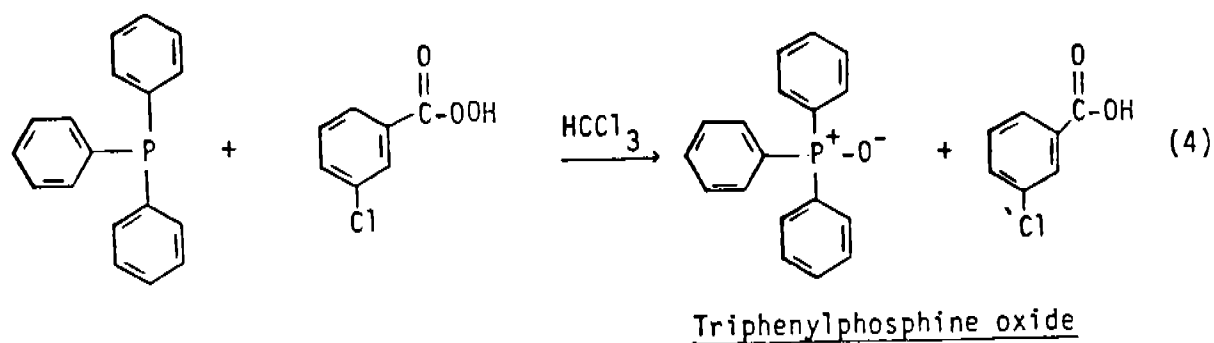
Dialkyl sulfoxides and sulfones have been prepared from the reaction of the appropriate alkyl halides with sodium sulfide under phase transfer catalytic conditions followed by subsequent mono- or dioxidation with m-chloroperbenzoic acid (Reaction 5).

$$(CH_3)_3C-CH_2-Cl \ + \ Na_2S \xrightarrow{\ (n\text{-}Bu)_4N^+Cl^-\ } (CH_3)_3C-CH_2-S-CH_2-C(CH_3)_3$$

(5)

Dineopentylsulfone

Dineopentylsulfoxide
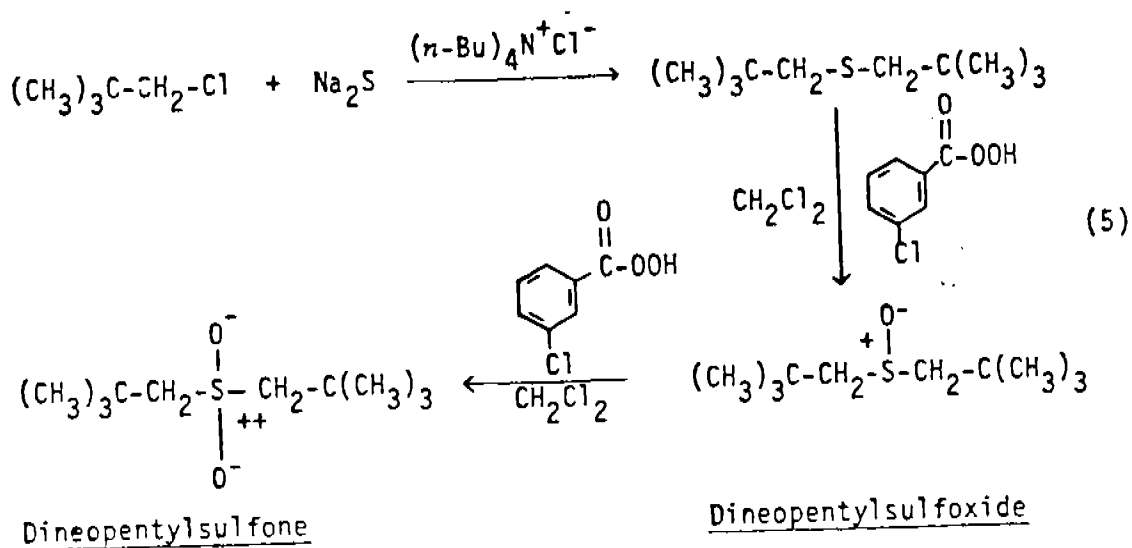
Trialkylamine oxides have been prepared from peracid oxidation of trialkylamines (Reaction 6).

(6)

Triisopropylamine oxide
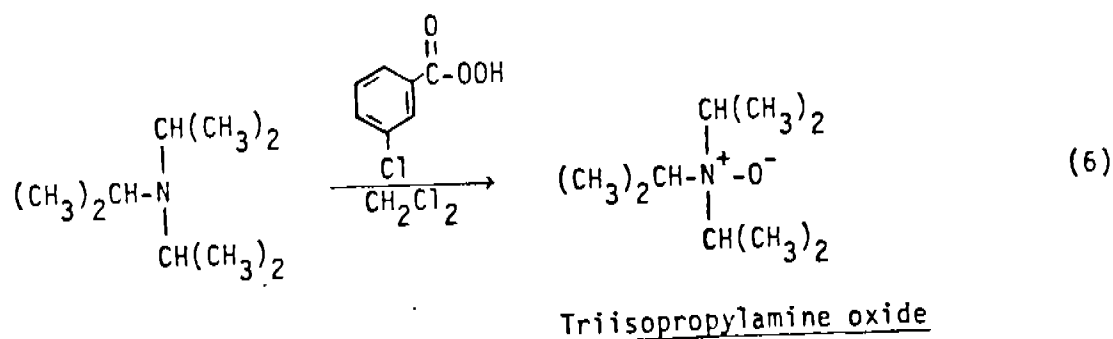
Quaternary ammonium and phosphonium salts have been prepared by a modification of the Brandstrom ion-pair extraction technique (reactions 7, 8, and 9, see refs 17 and 18).

$$(n\text{-Bu})_4N^+I^- + CH_3O\text{-}SO_2\text{-}OCH_3 \xrightarrow{CH_2Cl_2} (n\text{-Bu})_4N^+O^-SO_2OCH_3 + CH_3I \quad (7)$$

$$(n\text{-Bu})_4N^+O^-SO_2OCH_3 + H_2O \longrightarrow (n\text{-Bu})_4N^+HSO_3^- + CH_3OH \quad (8)$$

$$(n\text{-Bu})_4N^+HSO_3^- + \text{[arene-C-O}^-\text{Na}^+] \longrightarrow (n\text{-Bu})_4N^+ \text{[arene-COO}^-] + NaHSO_3 \quad (9)$$
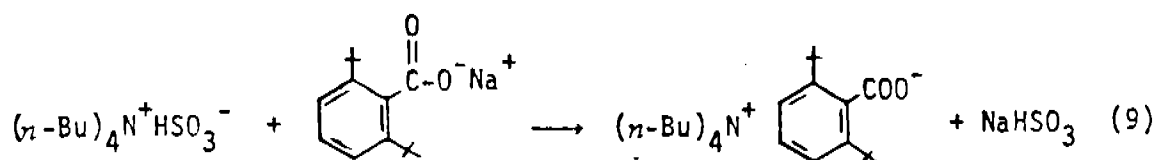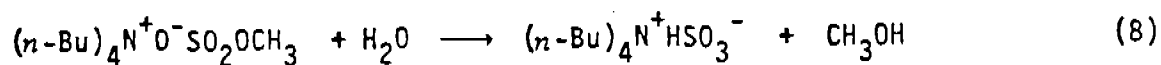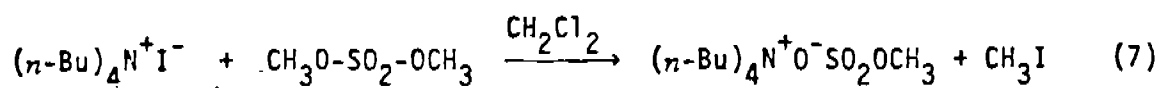
Tetra-n-butylammonium 2,6-di-t-butylbenzene

Dialkyphosphonates have been synthesized by means of the Arbuzov-Michalis reaction:

$$RO-\underset{OR}{\overset{OR}{P:}} + R\text{-Br} \xrightarrow{200^0} R-\underset{R}{\overset{O^-}{P^+}}-OR$$
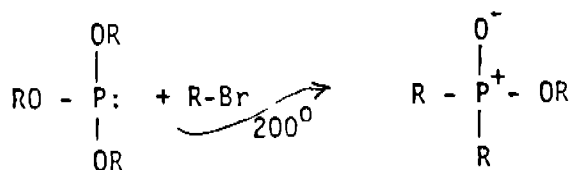
The mechanism for this transformation is outlined as follows:

$$(RO)_3 P: + R\text{-Br} \rightarrow R\text{-O-}\underset{OR}{\overset{OR}{P^+}}\text{-R} + Br^-$$

$$\downarrow$$

$$R\text{-O-}\underset{O^-}{\overset{OR}{P}}\text{-R} + R\text{-Br}$$
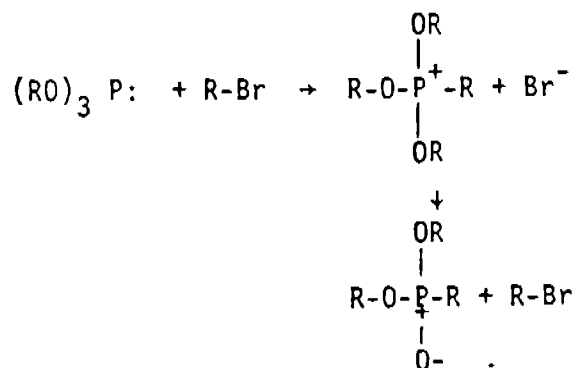
The alkylbromide is present solely as a catalyst. Using this approach,
a wide variety of alychalic diallyl phosphonates have been constructed.
For example:
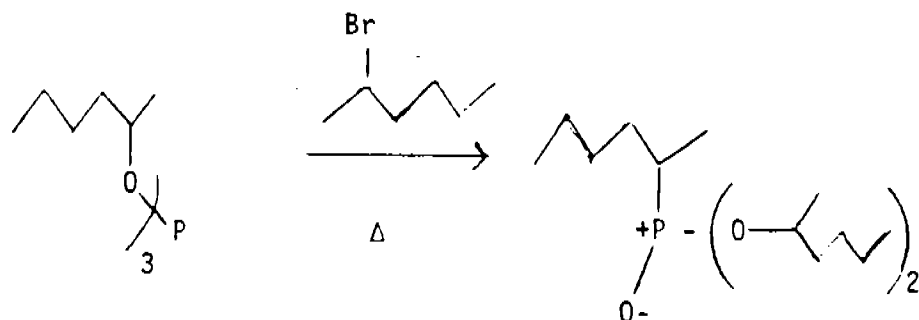
A series of long chain internal alcohols, diols, and trials have
been synthesized and tested. These extractants may be conveniently
synthesized from internal C-12 to C-18 alkenes produced commercially
from the teleperization of ethylene using a trialkylaluminum catalyst
followed by the isomerization of the terminal alkenes to a mixture of
internal alkenes. This source is available commercially and is
relatively inexpensive (about 20 cents per pound).

The following equations represent the methods by which the desired extractants have been synthesized:

(10) R—=—R' → 1. Oxo process 2. Reduction → R—CH(CH_2OH)—R'

(11) R—=—R' → dil. neut. MnO_4^- → R—(OH)(OH)—R'

(12) R—=—CH$_2$—R' → 1. allylic oxid. 2. hyd. 3. dil. nuet. MnO_4^- → R—(OH)(OH)—(OH)—R'
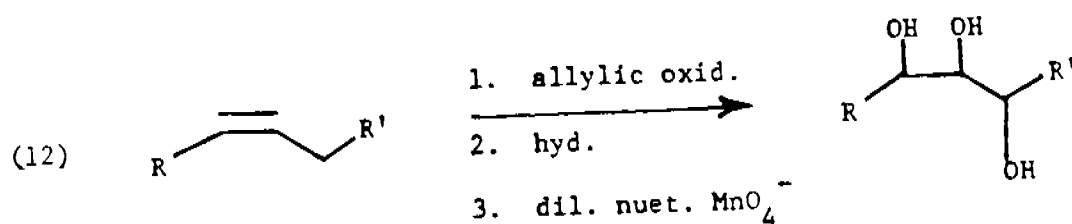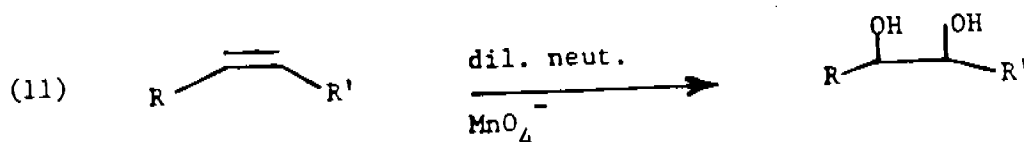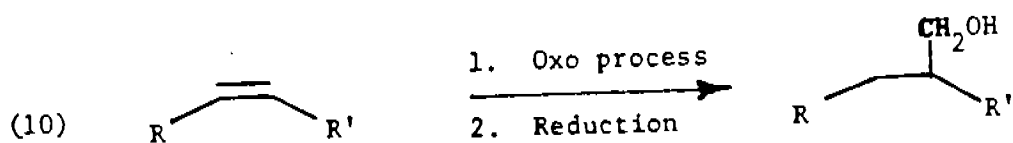
The product from reaction 10 prior to reduction is a mixture of aldehydes. These have been transformed to the corresponding oximes for evaluation as ethanol extractants.

(13) R—CH(HCO)—R' → H_2NOH → R—CH(HCNOH)—R'

3 DISCUSSION

The solubility curve titrations and the tie-line determinations
were carried out by a number of experimentors (see the acknowledgements)
and much of the apparent noise and/or bias in the expeimental data seems
to be a function of those individuals who made the measurements. For
example, Figs. 24-26 illustrate the reproducibility of the ethanol and
water distribution coefficients for three different solvent systems.
Each figure shows two sets, or runs, of observations that were completed
on different days and by different experimentors. The ethanol
distribution coefficients were computed in the first run from knowledge
of the mutual solubility curve, the feed mixture composition, and the
ethanol and water ratio in the organic phase. In the second run, they
were computed from the simultaneous solution of three material balance
equations, but the solubility curve was only used to estimate the weight
fraction of the solvent in the equilibrated raffinate.

In the first run cases (Figs. 24-26), the water distribution
coefficients were estimated from knowledge of the organic ethanol weight
fraction and by projecting graphically from the solubility curve. In
the second runs, the water distribution coefficients were determined
from the simultaneous solution of three material balance equations. In
these latter cases, the solubility curve was used only to estimate the
weight fraction of solvent in the equilibrated raffinate. All other
ethanol-to-water ratios and separation factors were calculated directly
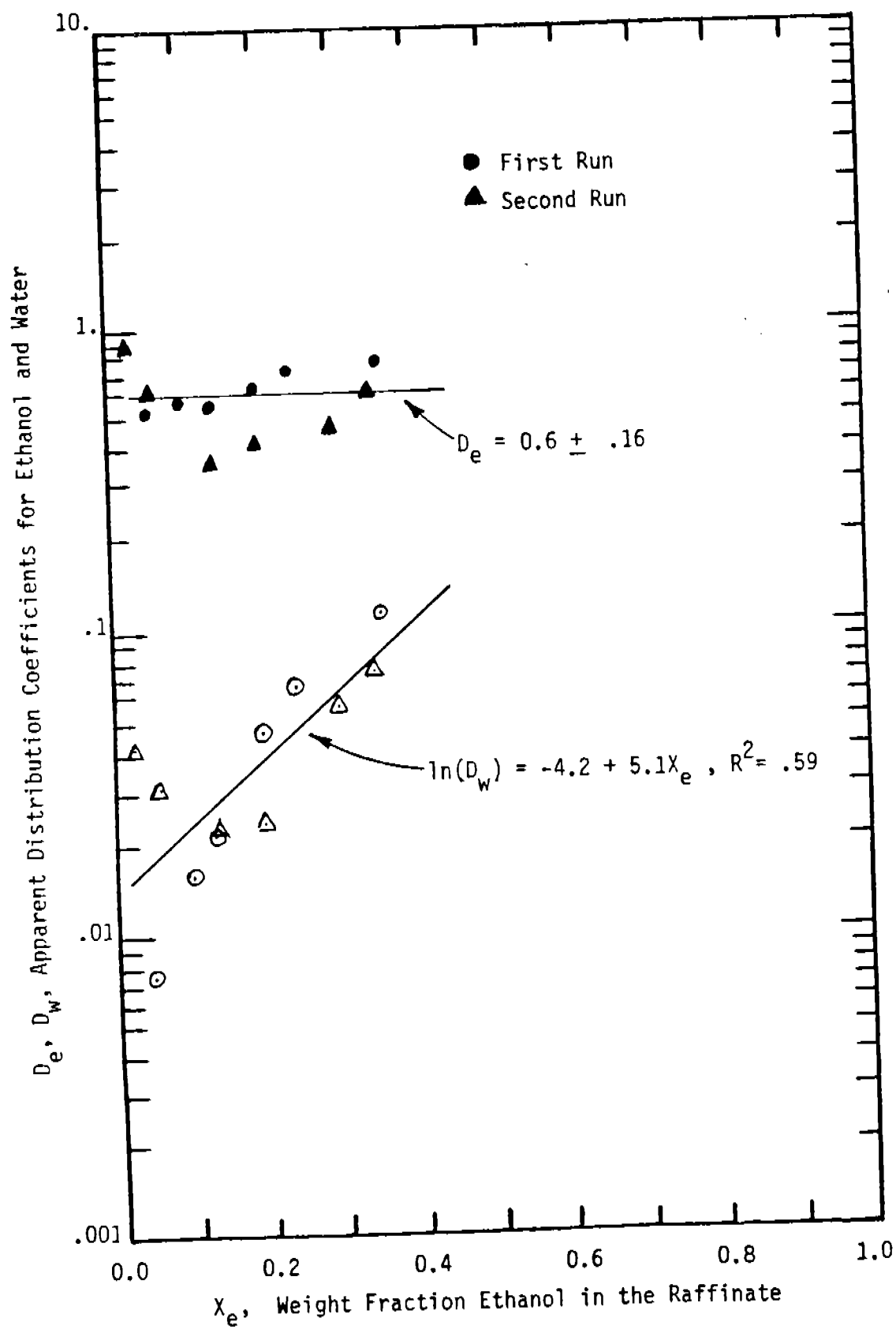
Fig. 24. Distribution coefficients for ethanol and water using 50 vol % tridecyl alcohol in 2-octanol as the solvent.

Fig. 25. Replicate evaluations of the distribution coefficients for ethanol and water using the solvent 50 vol % tridecyl alcohol in NORPAR-12.

Fig. 26 Distribution coefficients for ethanol and water using 25 vol % 2-ethylhexanol, 25 vol % tridecyl alcohol in ISOPAR-G.

The figure plots D_e, D_w, Apparent Distribution Coefficients for Ethanol and Water (vertical log axis from .001 to 10.) versus X_e, Weight Fraction Ethanol in the Raffinate (horizontal axis from 0.0 to 1.0).

Legend:
▲ First Run, No Organic Injections
● Second Run, Organic Injections

$D_e = 0.5 \pm 0.12$

$\ln(D_w) = -5.8 + 6.25X_e$

$R^2 = .93$

from GC analysis as discussed in more detail in section 2.2 of this report.

The apparent noise and/or bias associated with the ethanol distribution coefficients in Figs. 24 thru 26 tends to increase with decreasing equilibrium ethanol concentrations in the raffinates. This result is probably due mostly to the fact that the ethanol weight fractions in the initial and equilibrium aqueous phases were lower and; therefore, the relative errors in the measurements are larger. For this reason, the three outliers in Fig. 25 (i.e. the second run with less than 0.2) were not included in the correlation. In addition, the errors tend to be larger in systems such as kerosene and pure NORPAR-12 (see Figs. 30 and 31) where the ethanol and water distribution coefficients are very small and their organic concentrations are relatively difficult to measure. that is shown.

Although the water distribution coefficients for most systems (see Figs. 27-+5) are clearly functions of the aqueous ethanol concentrations, in many cases it is not clear whether or not the ethanol distribution coefficients are truly dependent upon the ethanol concentrations in the raffinate. Statistically, the data often tend 83 to support the opposite conclusion that the ethanol distribution coefficients are essentially constant (e.g.
Figs. 24-26, 31, 33, 34, and 37) for all equilibrium concentrations in the raffinate. This conclusion was also arrived at by Roddy [19,2] who used radioactive tracers to characterize a number of candidate extractants.

$\ln(D_e) = -0.5 + X_e$, $R^2 = .56$

$\ln(D_w) = -4.1 + 7.3X_e$, $R^2 = .91$

D_e, D_w, Apparent Distribution Coefficients for Ethanol and Water

X_e, Weight Fraction Ethanol in the Raffinate
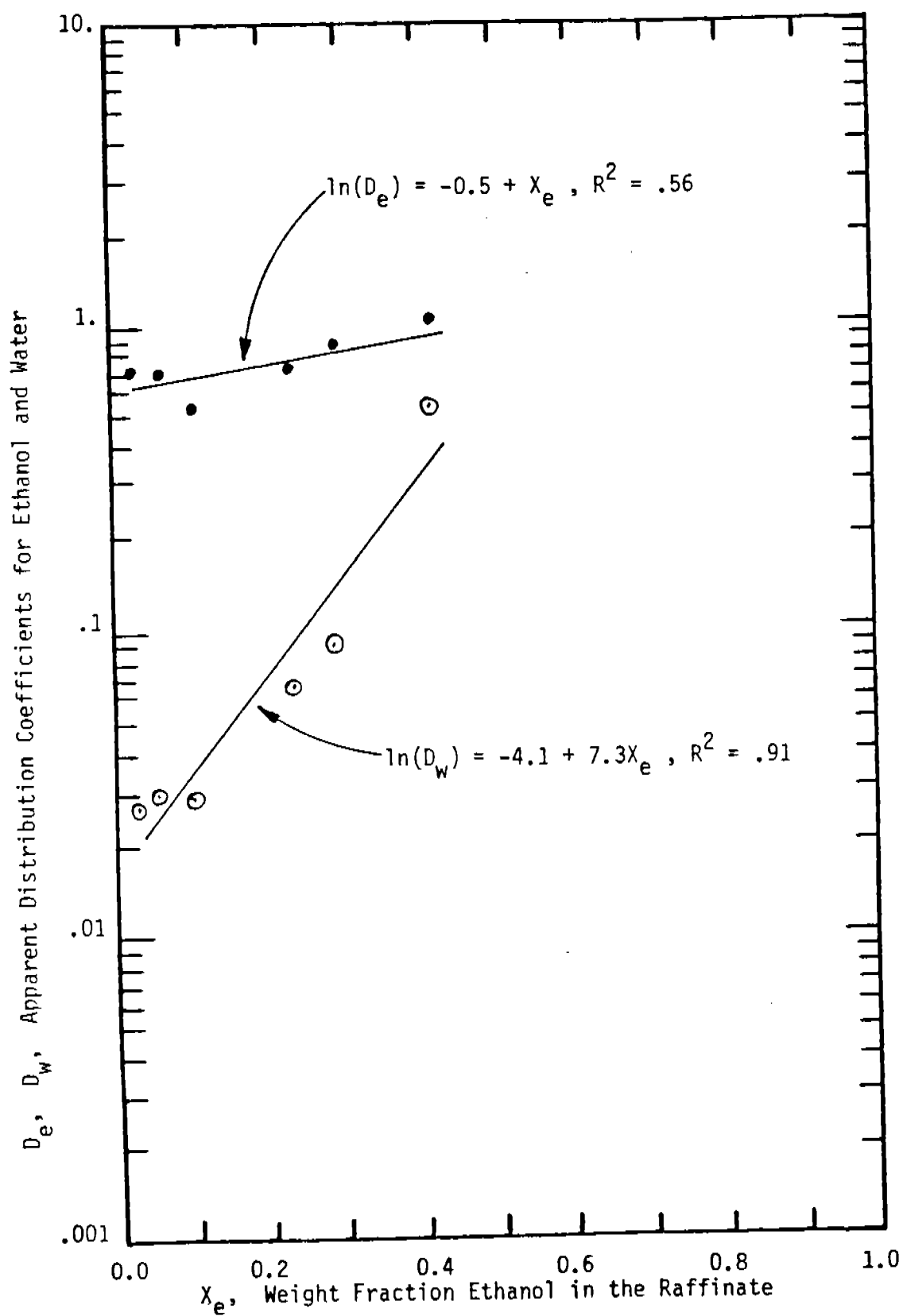
Fig. 27. Distribution coefficients for ethanol and water using 2-ethyl hexanol as the solvent.
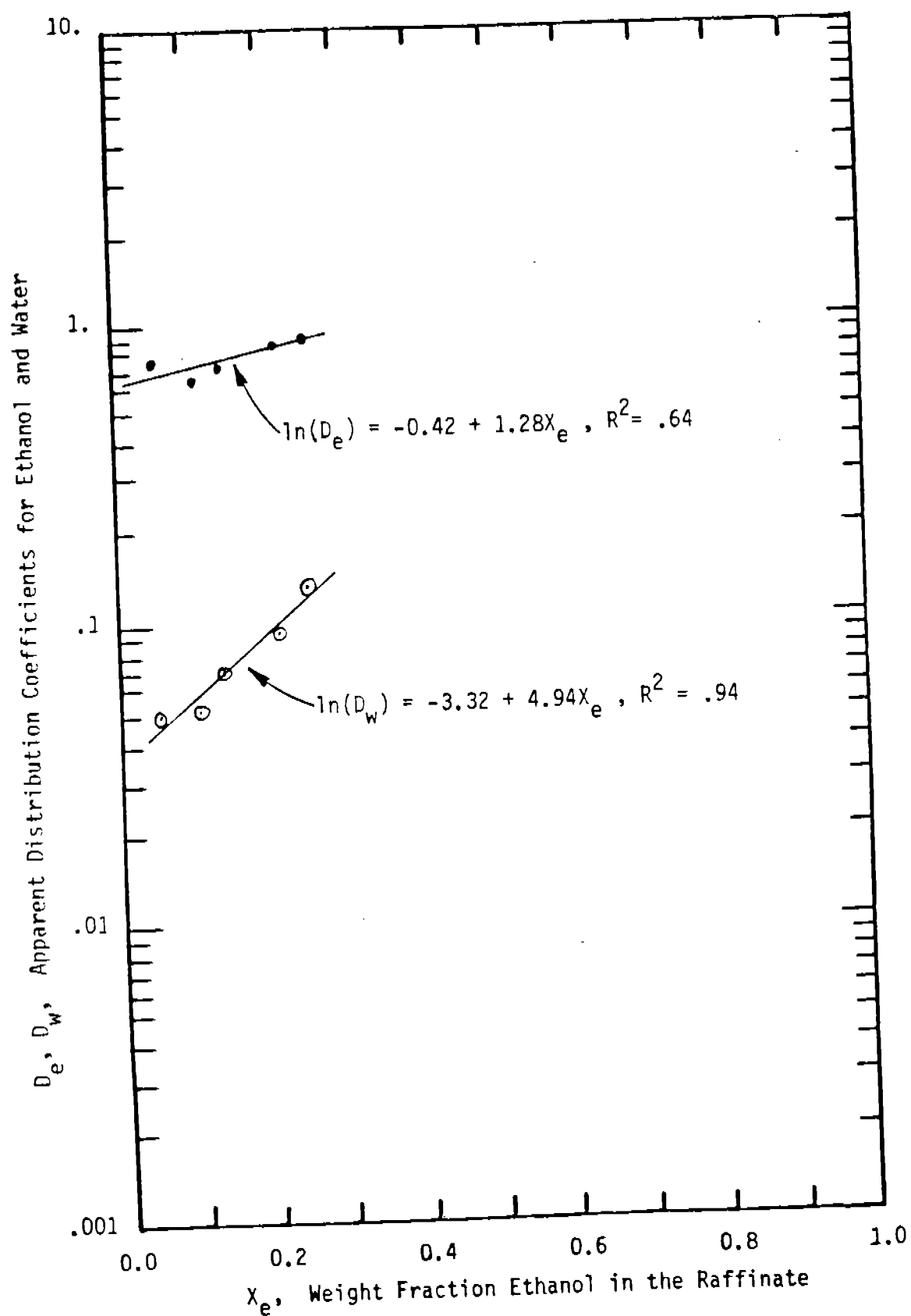
Fig. 28. Distribution coefficients for ethanol and water using 2-octanol as the solvent.
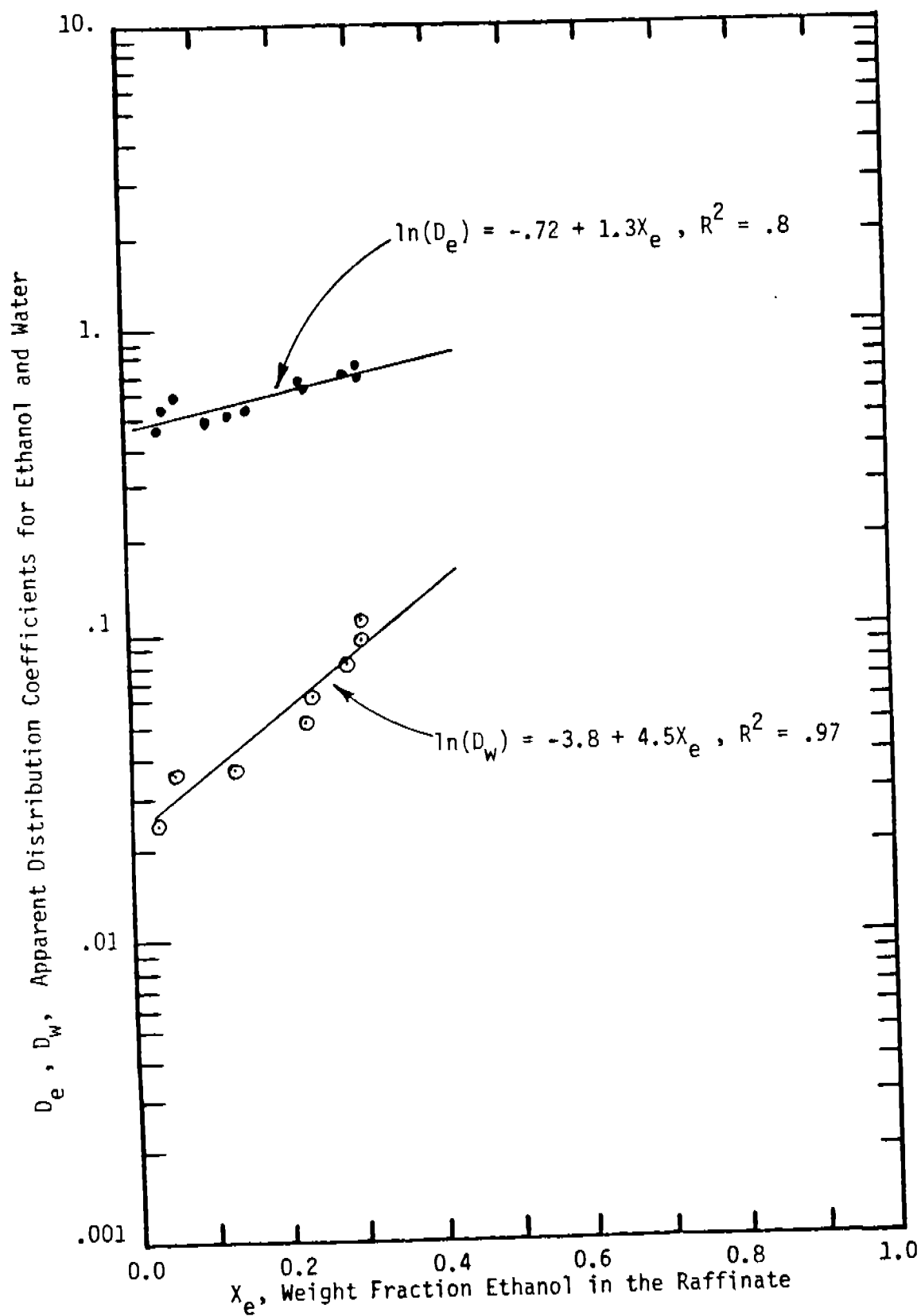
Fig. 29. Distribution coefficients for ethanol and water using decyl alcohol as the solvent.
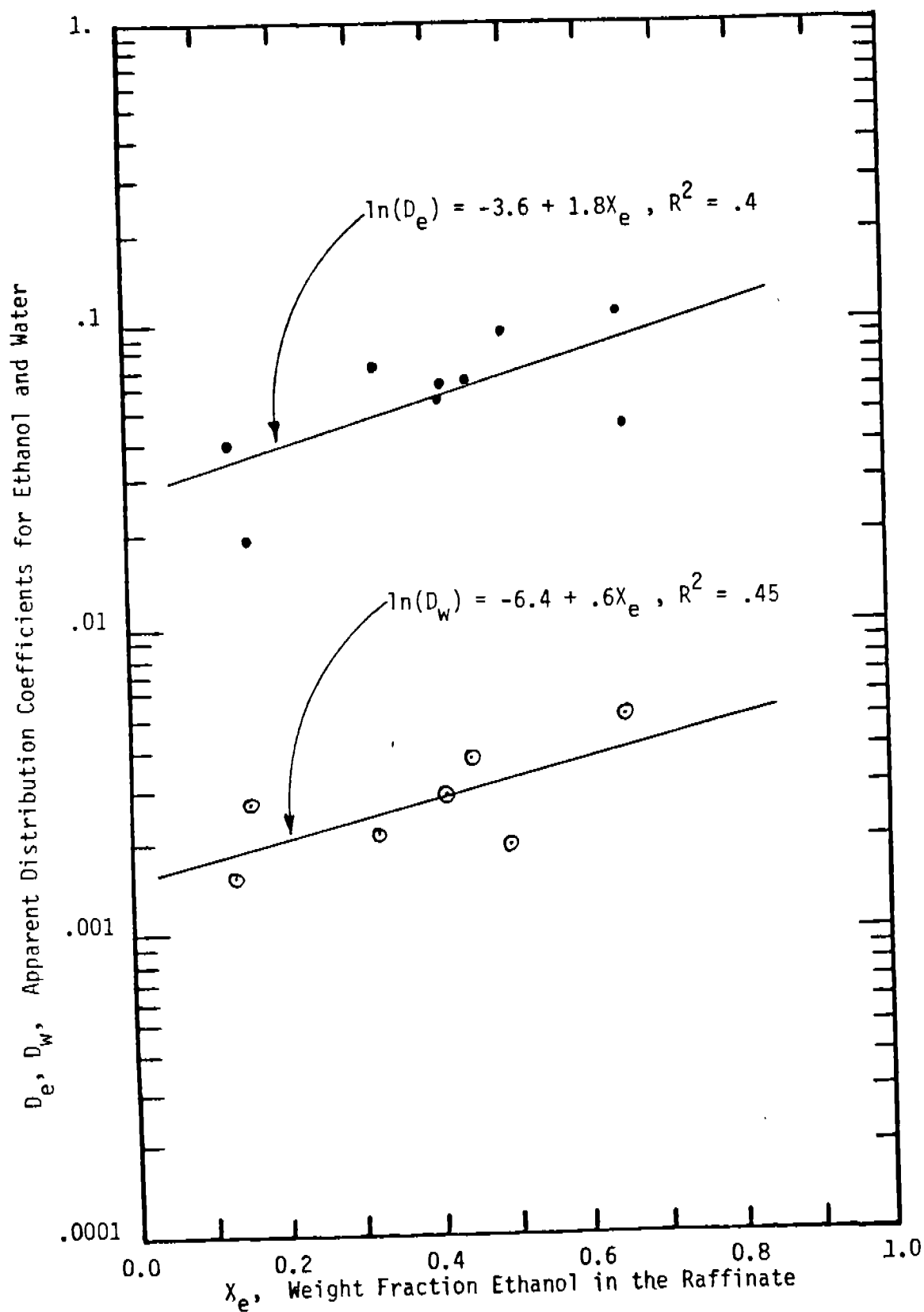
Fig. 30. Distribution coefficients for ethanol and water extraction using kerosene as the solvent.

Fig. 31. Distribution coefficients for ethanol and water using NORPAR-12 as the solvent.
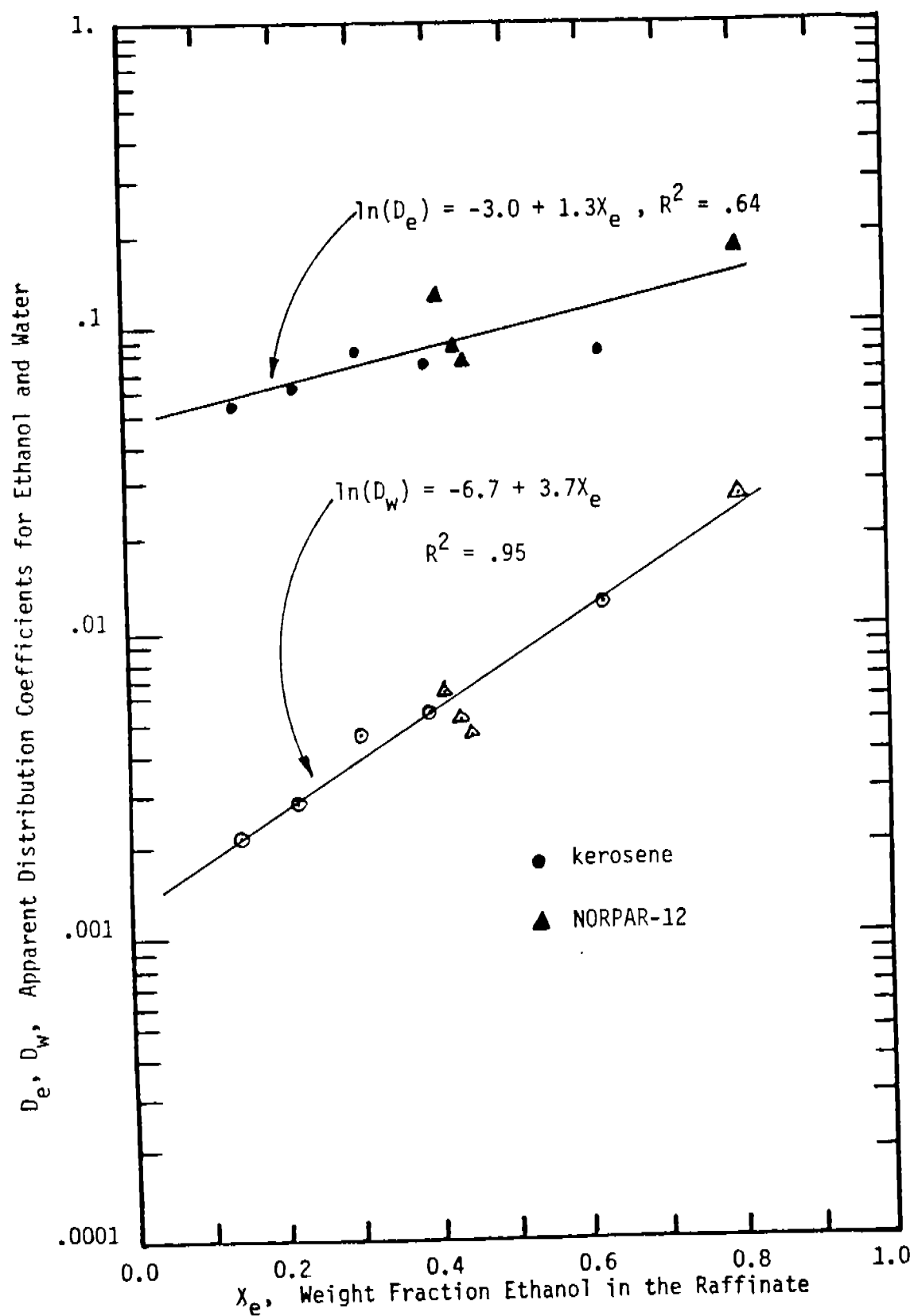
Fig. 32. Distribution coefficients for ethanol and water extraction using 10 vol % tridecyl alcohol in either kerosene or NORPAR-12.
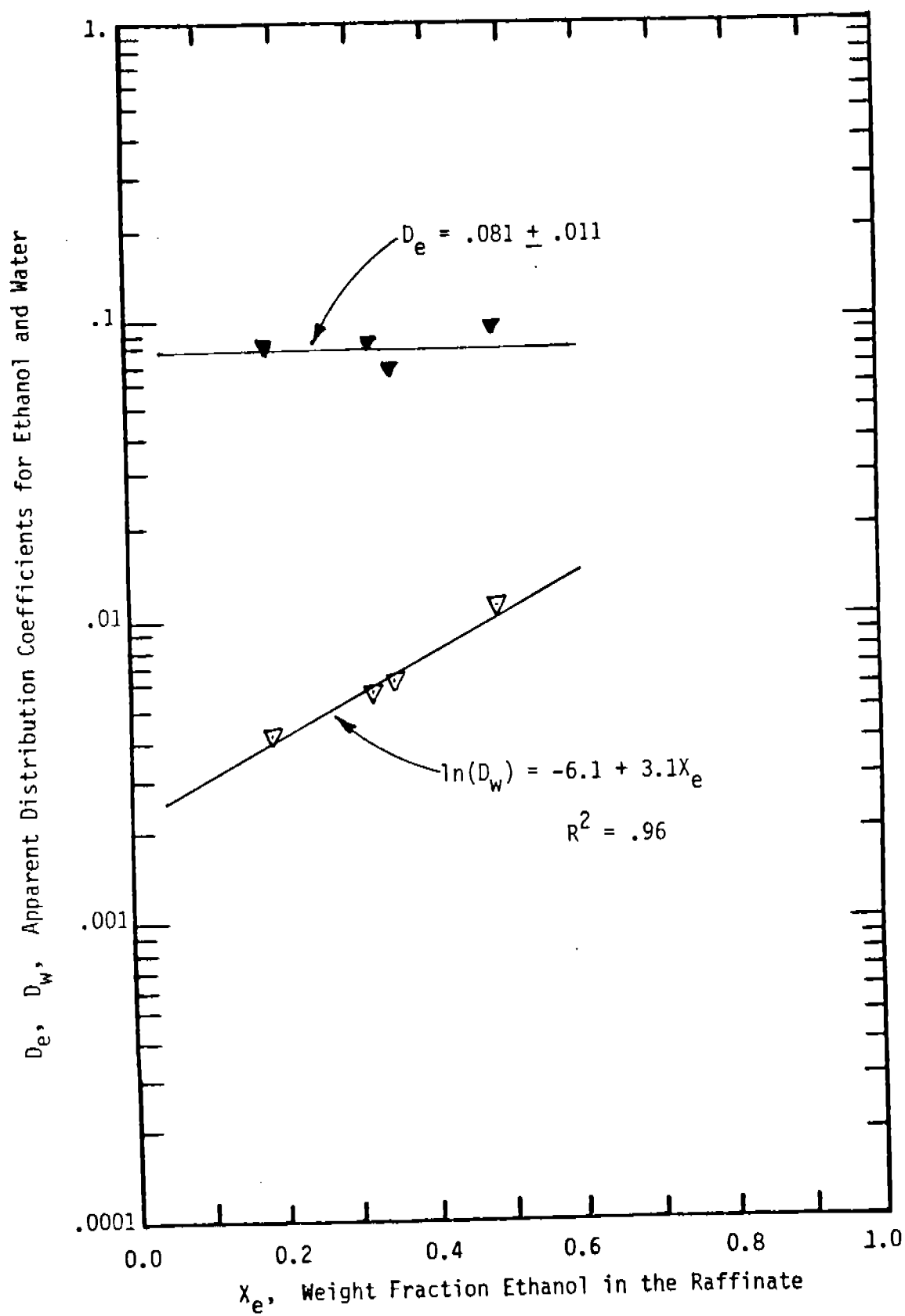
Fig. 33. Distribution coefficients for ethanol and water extraction using the solvent 10 vol % p-dodecyl phenol in n-dodecane.
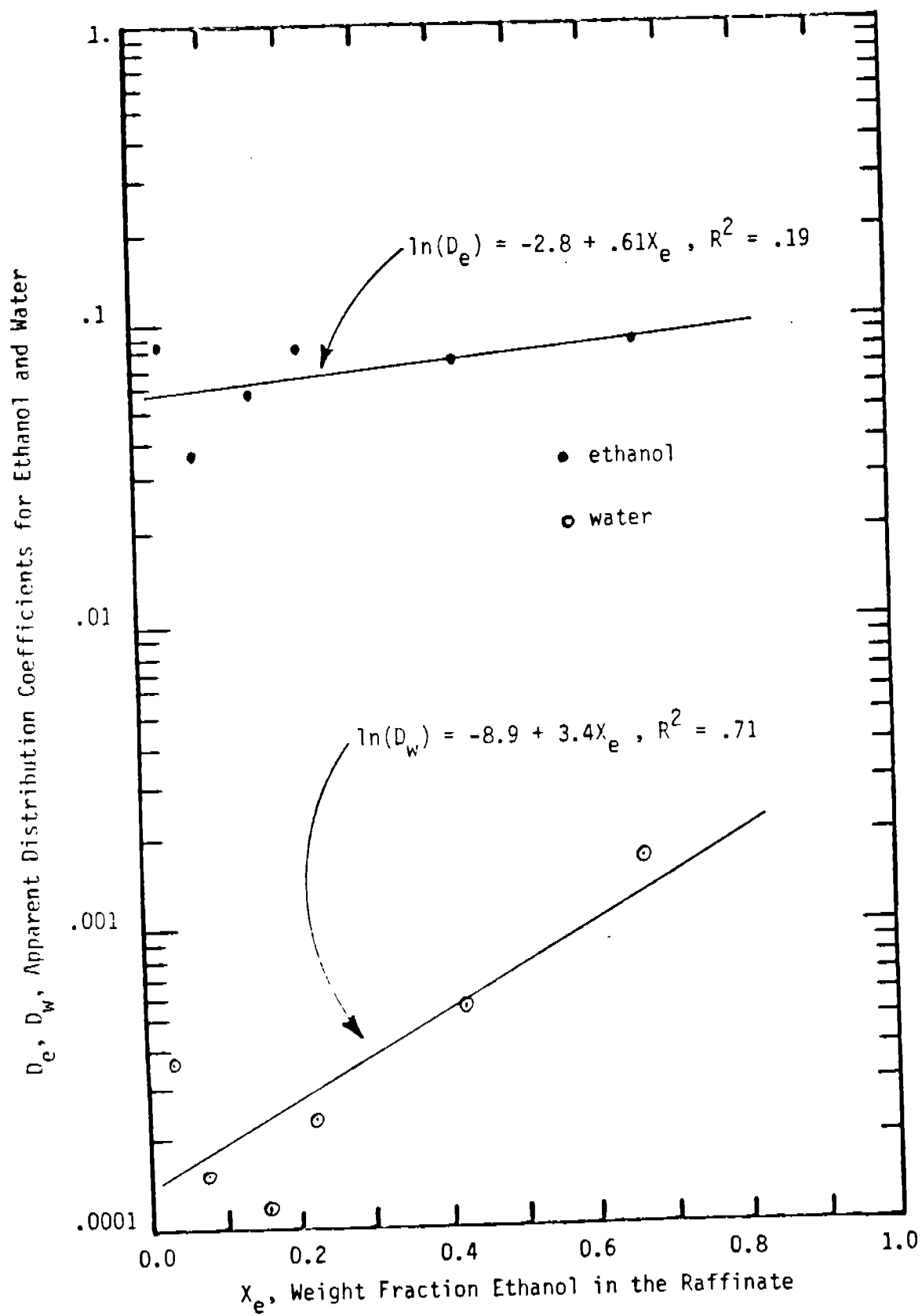
Fig. 34 Distribution coefficients for ethanol and water using 10 vol % dodecyl alcohol in NORPAR-12 as the solvent.

The y-axis is labeled "D_e, D_w, Apparent Distribution Coefficients for Ethanol and Water" with values from .0001 to 1.

The x-axis is labeled "X_e, Weight Fraction Ethanol in the Raffinate" with values from 0.0 to 1.0.

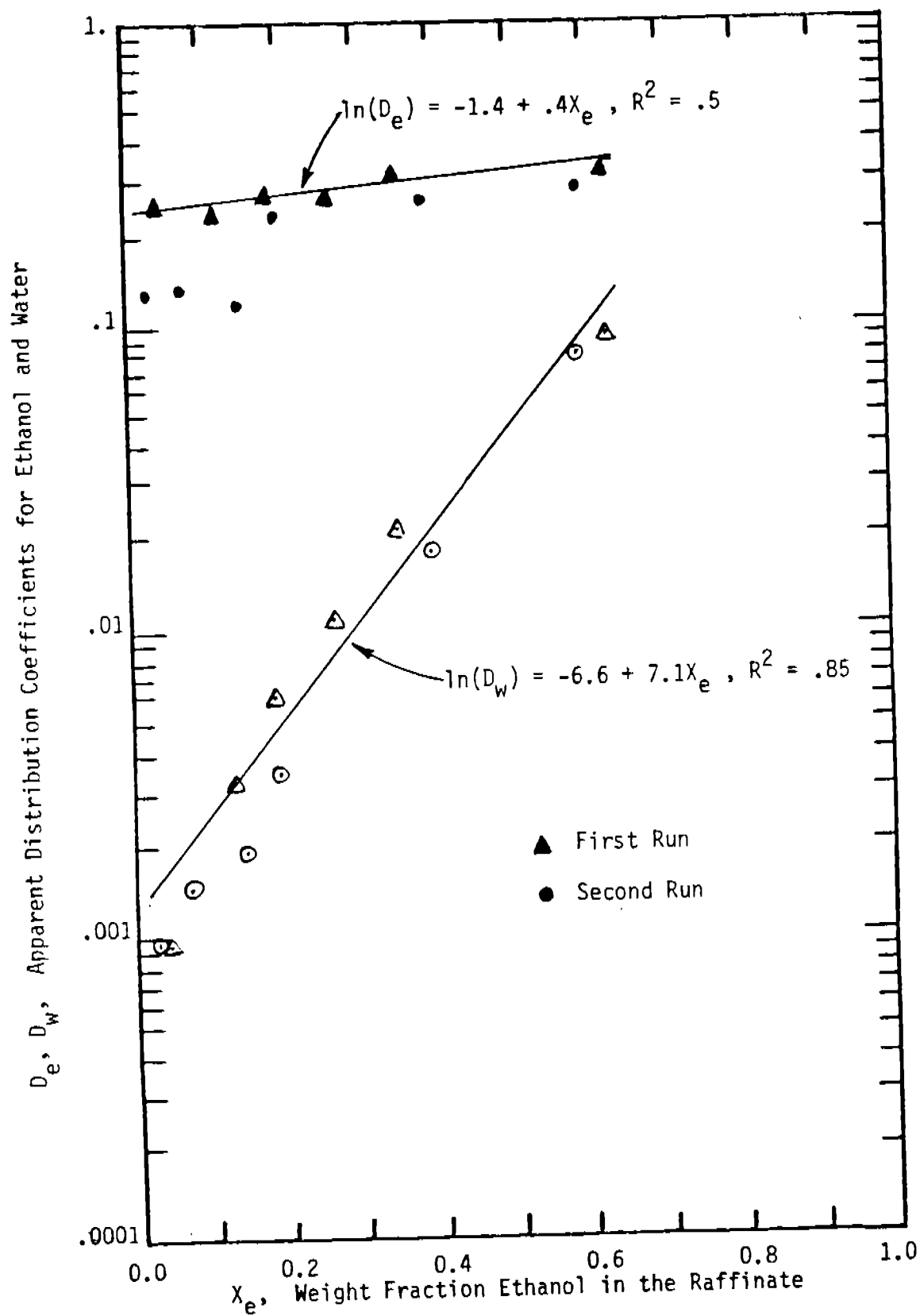$$\ln(D_e) = -2.2 + 1.5X_e, \quad R^2 = .6$$

$$\ln(D_w) = -9. + 8.3X_e$$
$$R^2 = .88$$
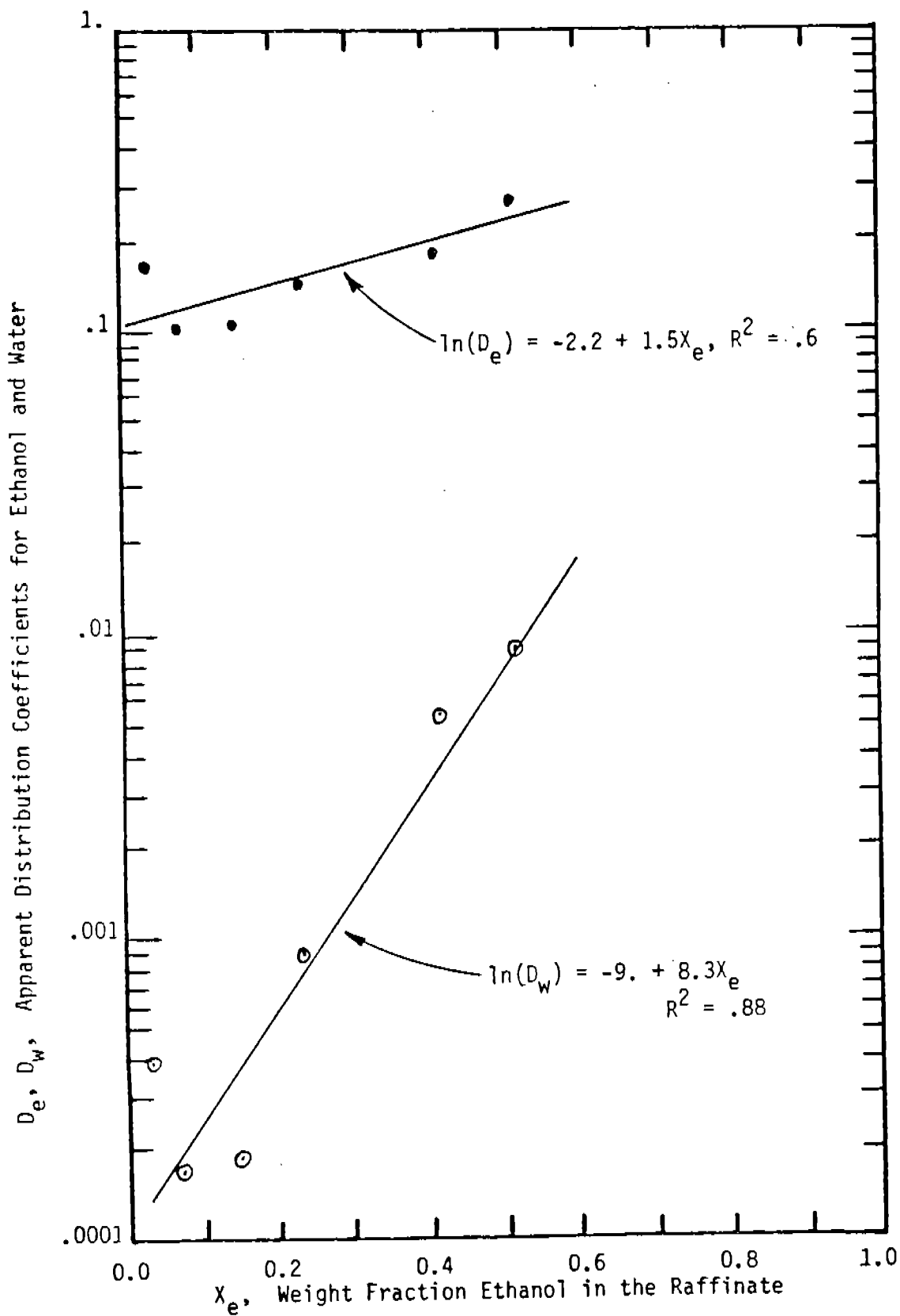
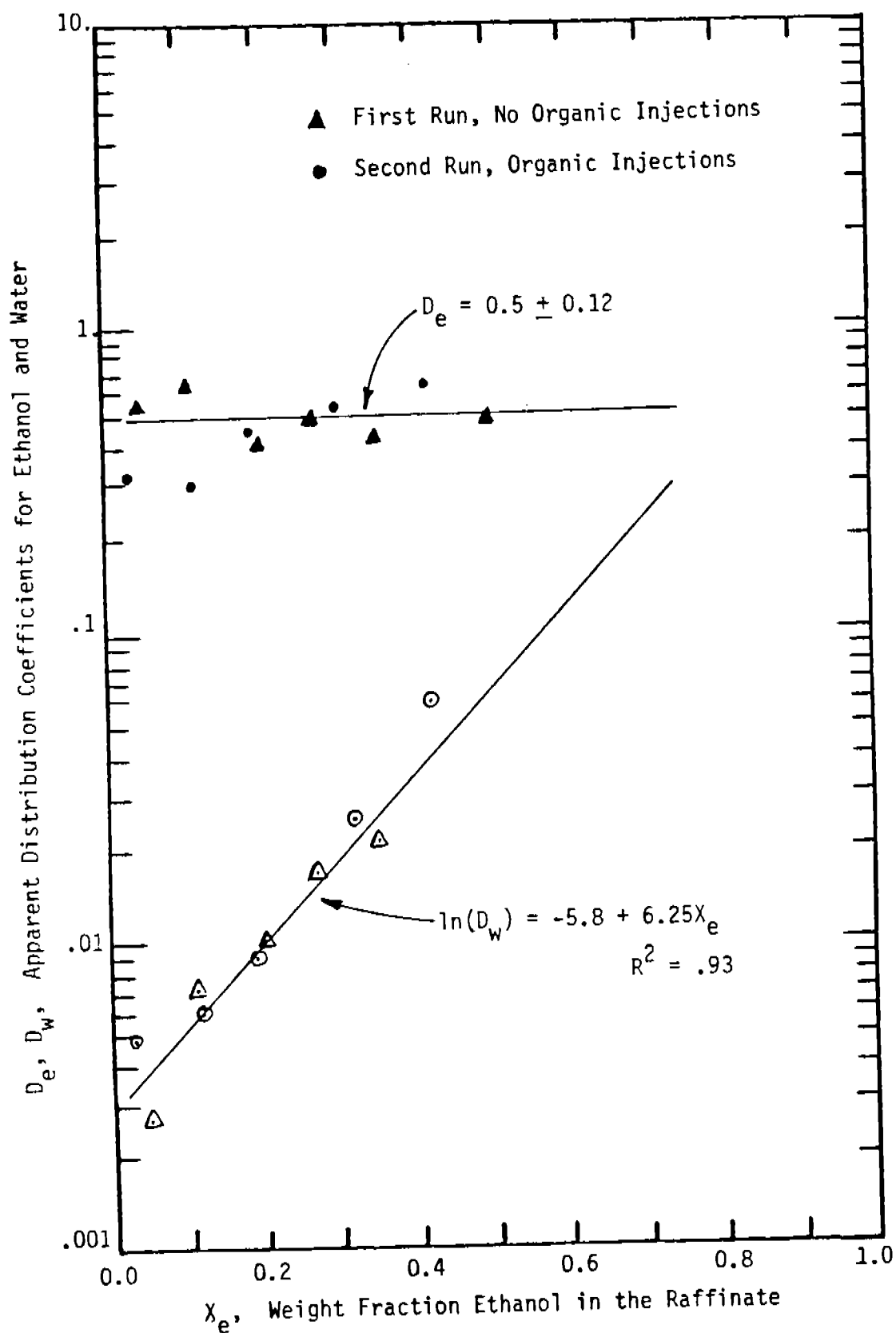Fig. 35. Distribution coefficients for ethanol and water using the solvent 20 vol % tridecyl alcohol in NORPAR-12.
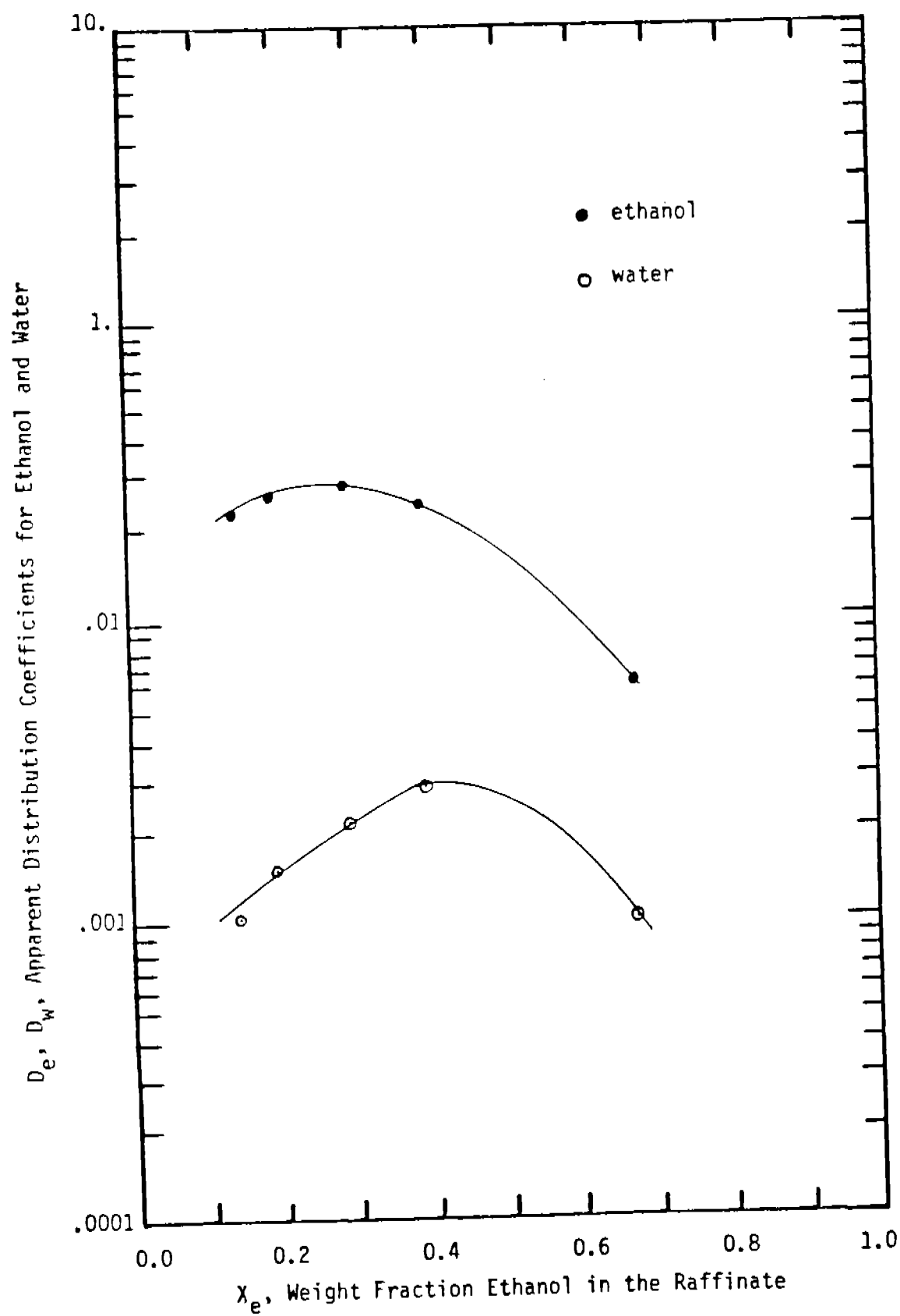
Fig. 36 Distribution coefficients for ethanol and water using 30 vol %
tri-n-butyl phosphate in NORPAR-12 as solvent.
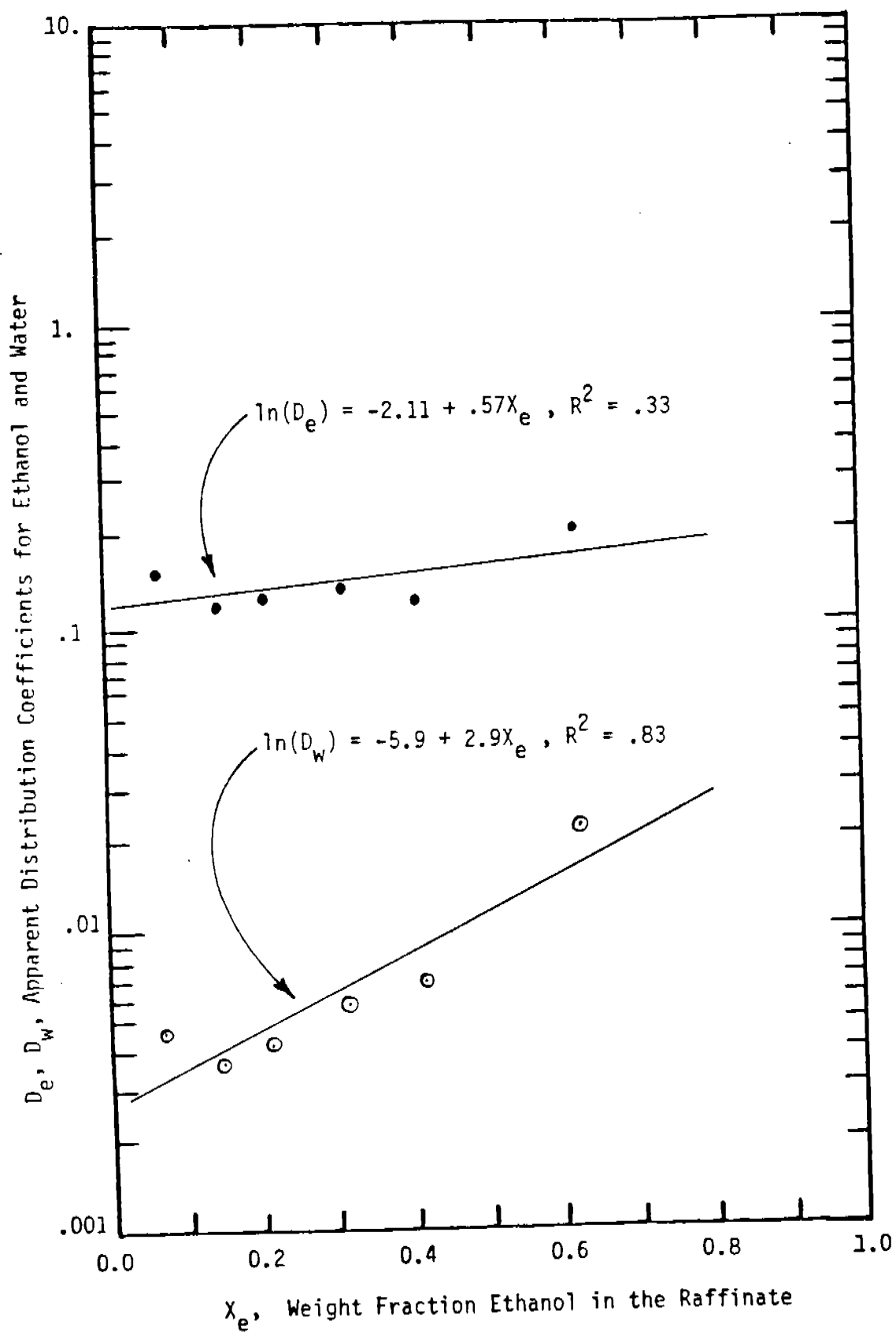
Fig. 37 Distribution coefficients for ethanol and water using the solvent 30 vol % di-2-ethylhexyl, 2-ethylhexyl phosphonate in NORPAR-12.
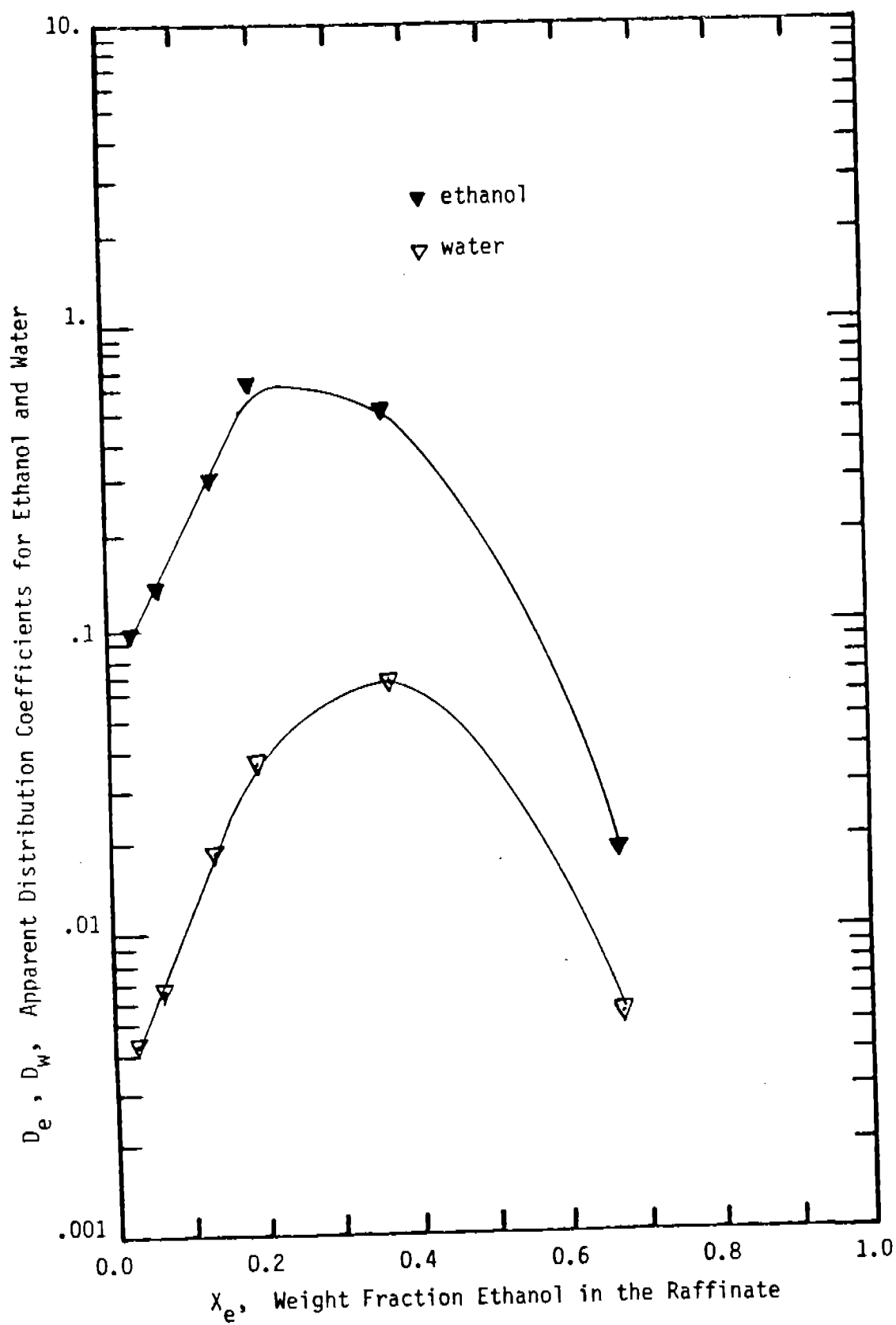
Fig. 38. Distribution coefficients for ethanol and water extraction using the solvent 50 vol % 2-ethylhexanol in ISOPAR-G.
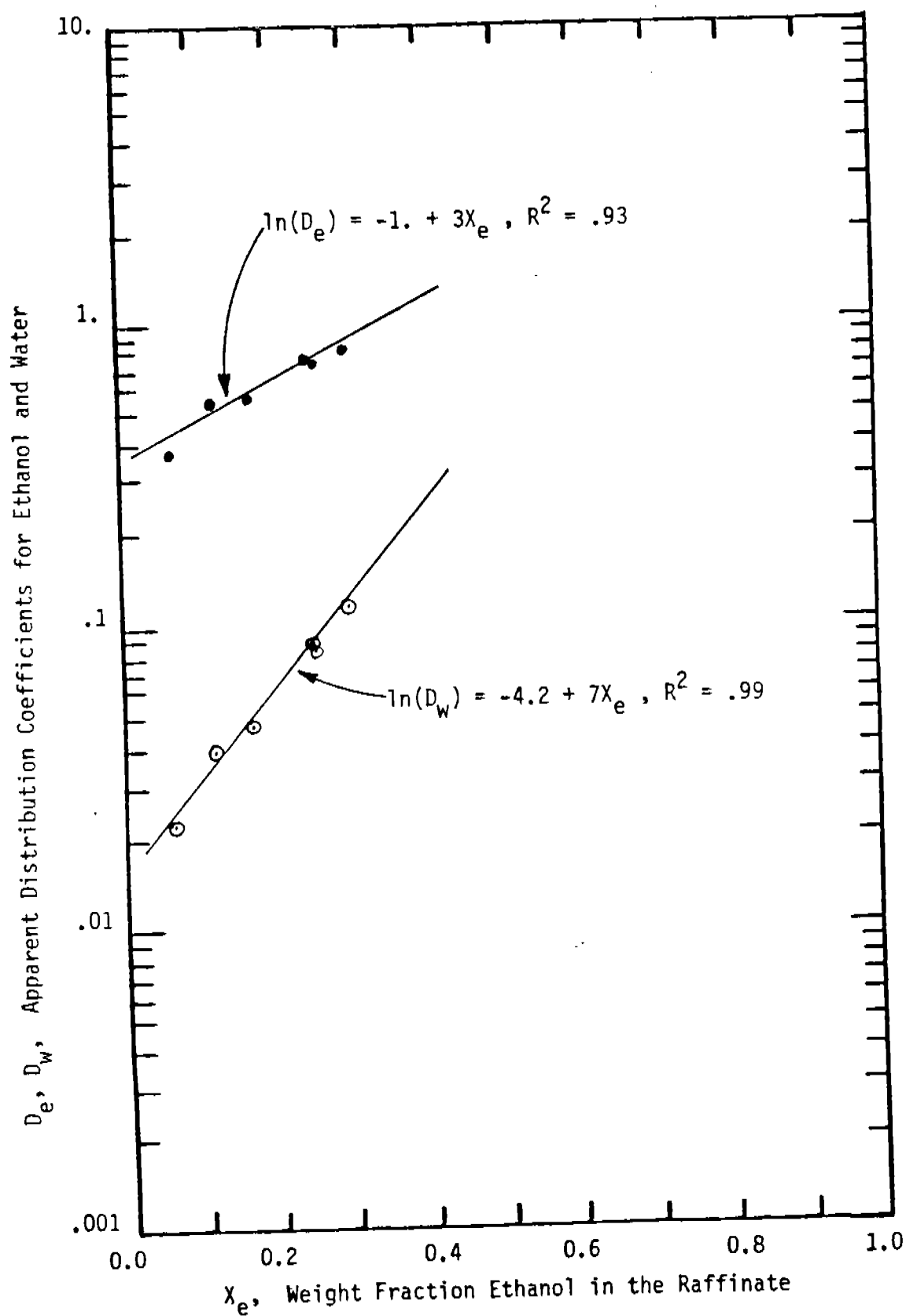
Fig. 39. Distribution coefficients for ethanol and water extraction using the solvent 50 vol % Conoco diol in 2-ethylhexanol.

The y-axis is labeled: D_e, D_w, Apparent Distribution Coefficients for Ethanol and Water

The x-axis is labeled: X_e, Weight Fraction Ethanol in the Raffinate

$$\ln(D_e) = -1.34 + 2.27X_e, R^2 = .66$$

$$\ln(D_w) = -9.15 + 18.3X_e, R^2 = .93$$
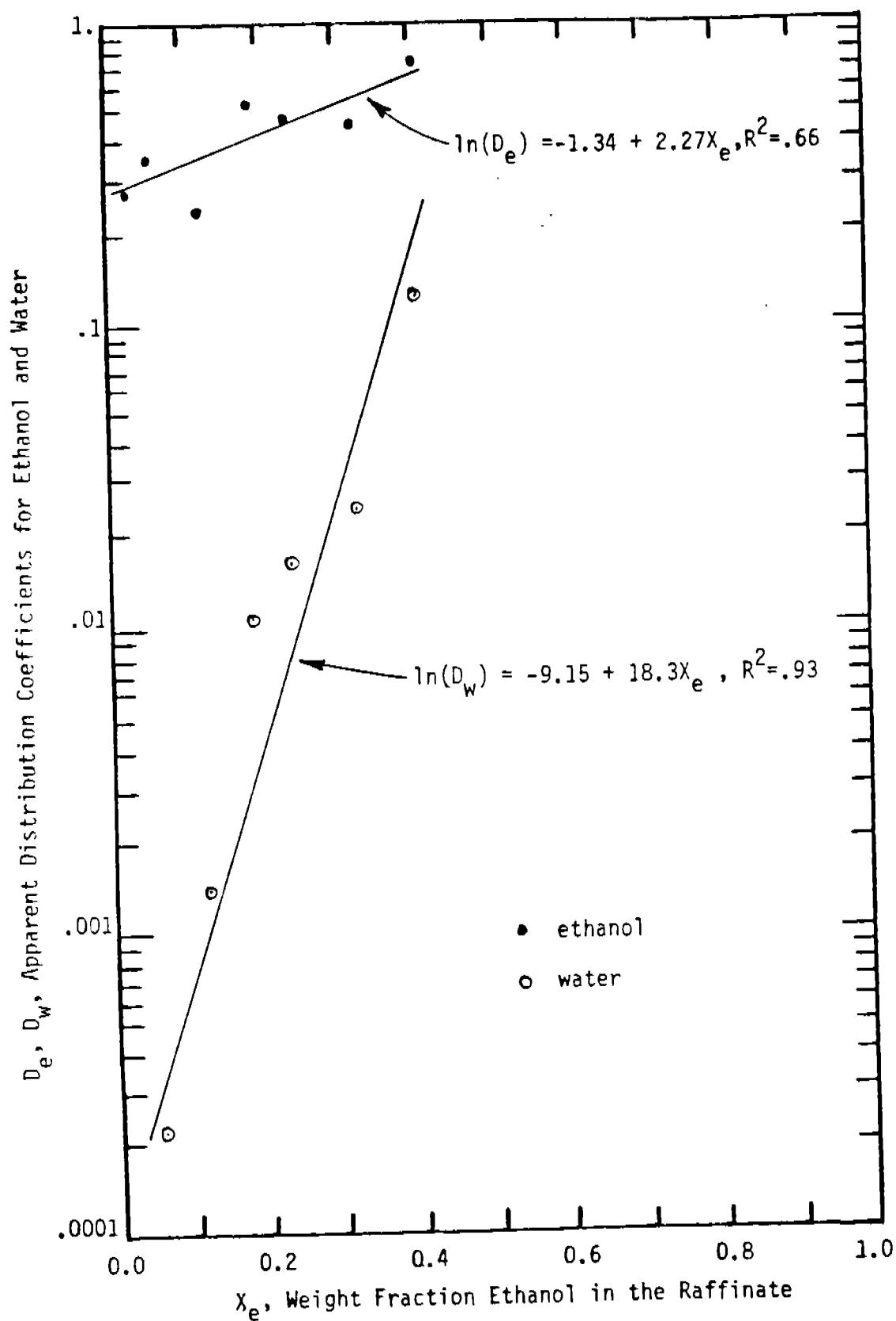
● ethanol

○ water

Fig. 40   Distribution coefficients for ethanol and water using 50 vol %
tridecyl alcohol in tetrachloroethane.
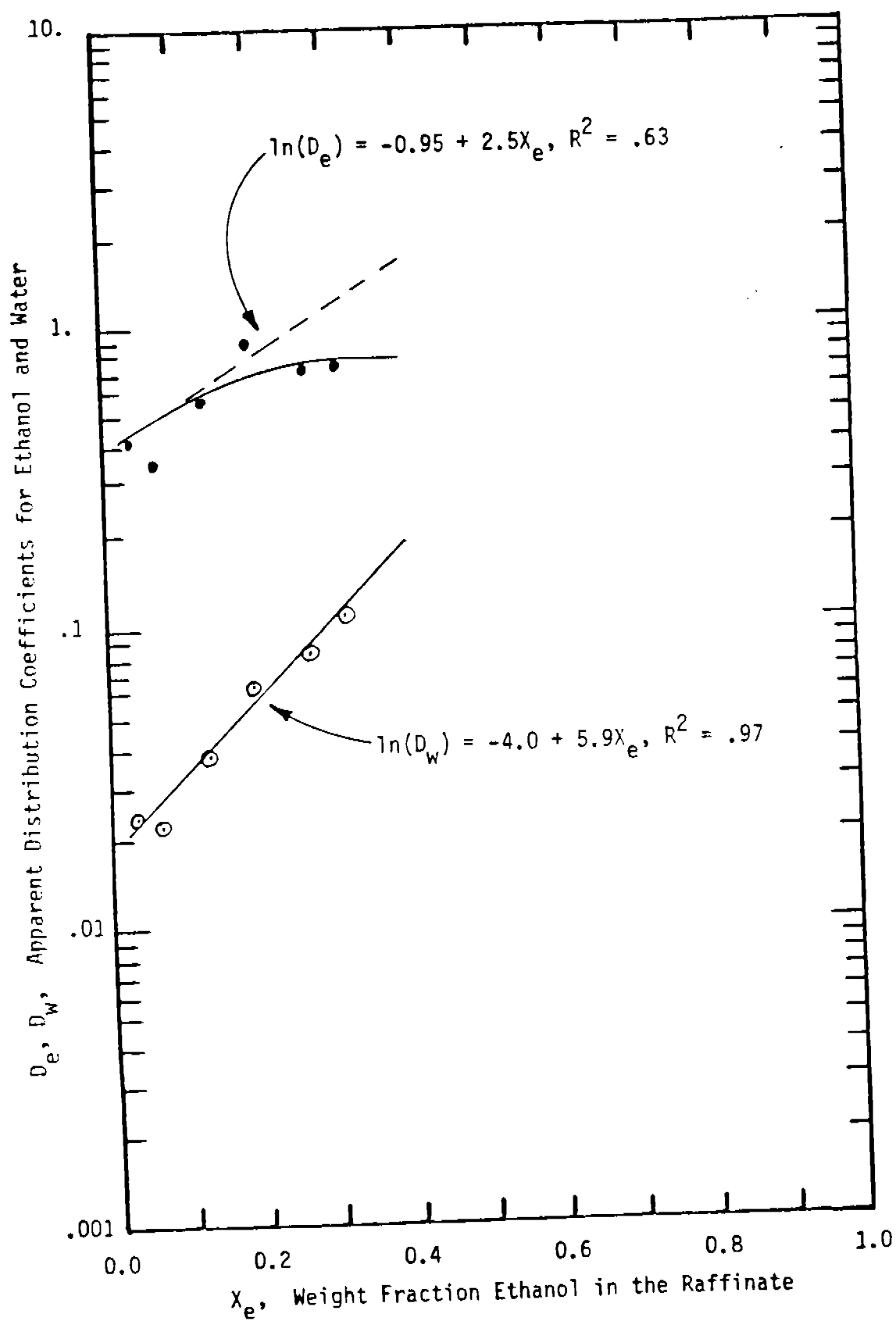
Fig. 41 Distribution coefficients for ethanol and water using 50 vol % tridecyl alcohol in 2-ethyhexanol.
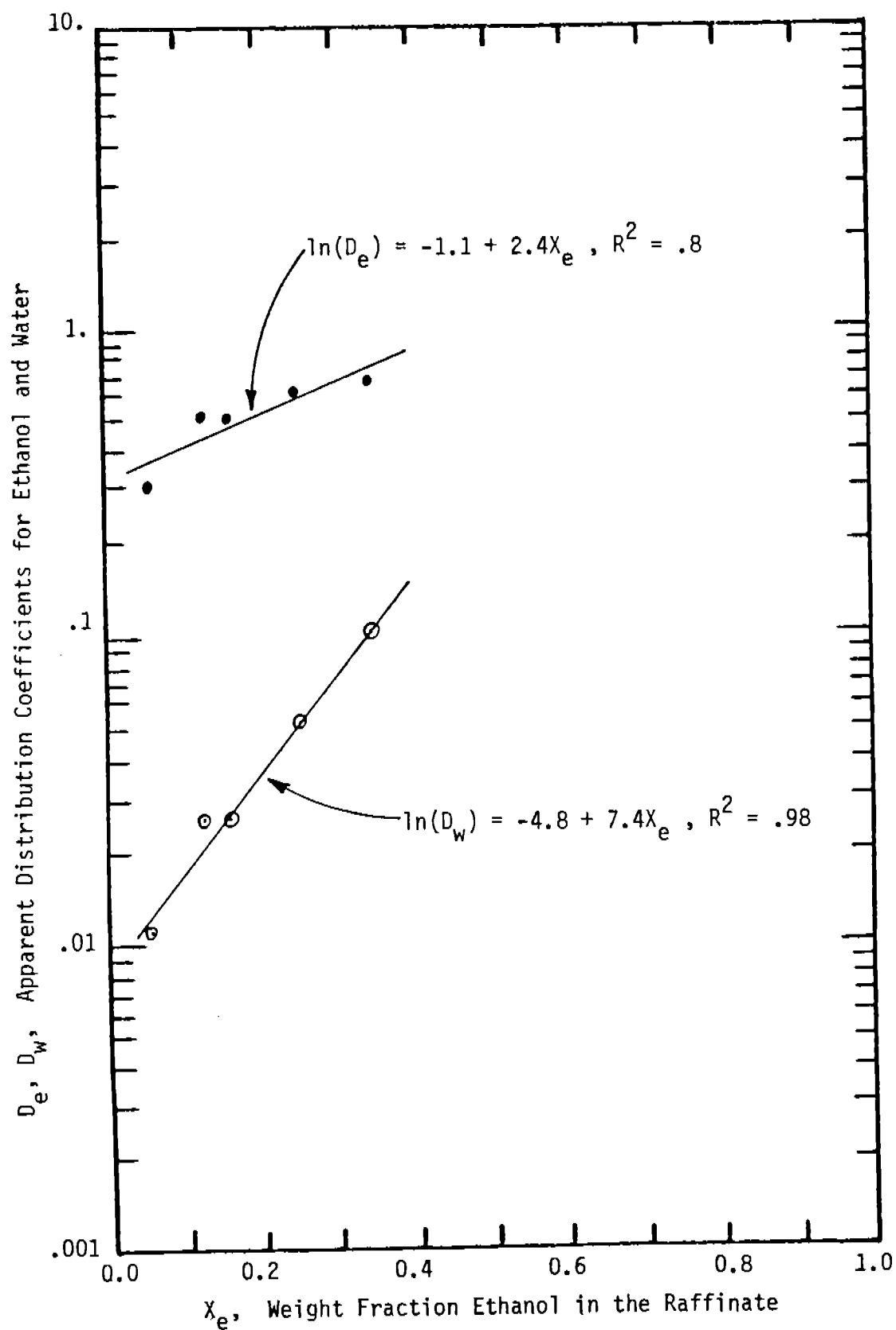
Fig. 42. Distribution coefficients for ethanol and water extraction into the solvent 70 vol % tridecyl alcohol in 2-ethylhexanol
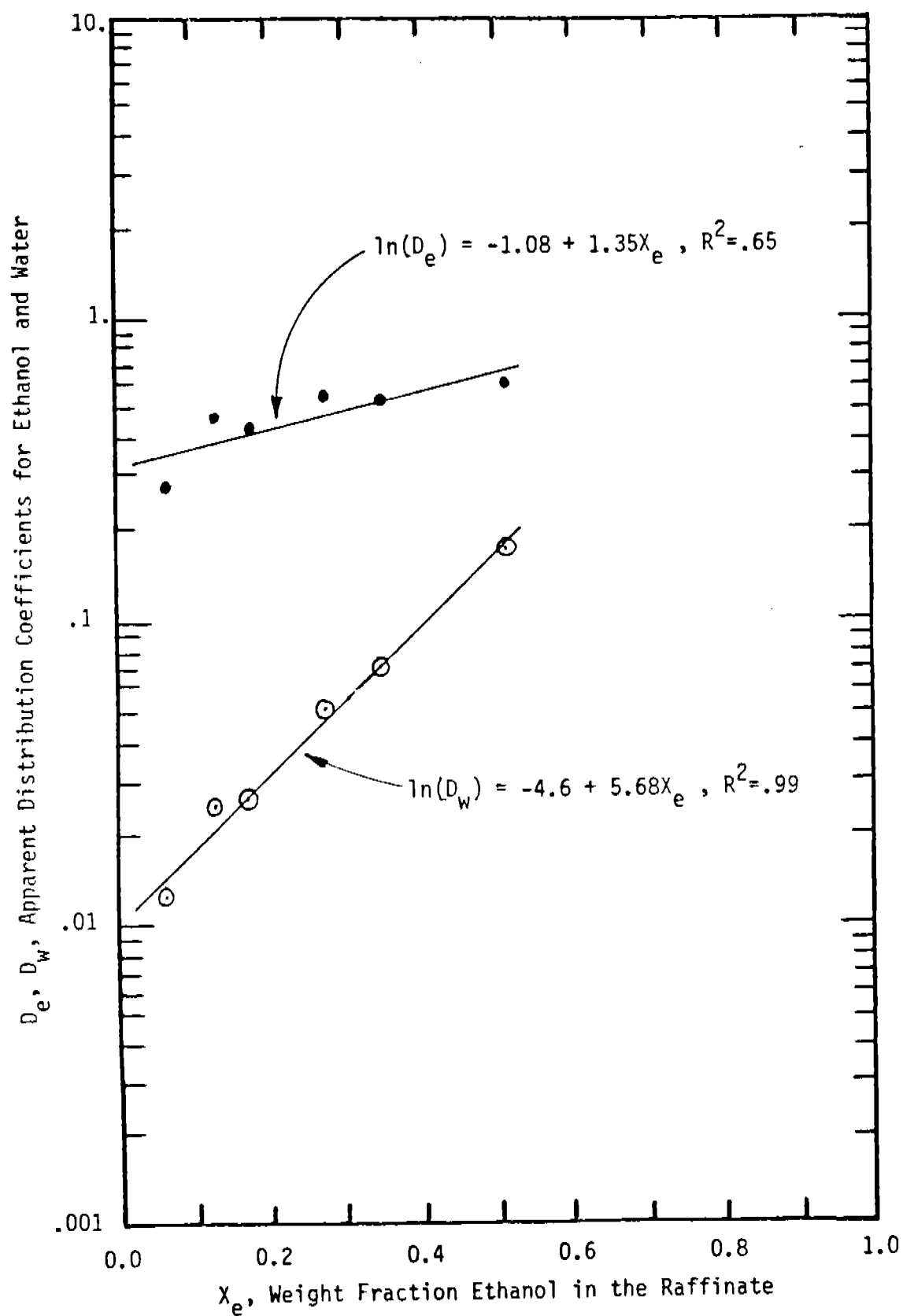
Fig. 43   Distribution coefficients for ethanol and water using 30 vol % NORPAR-12, 35 vol % 2-ethylhexanol and tridecyl alcohol as the solvent.
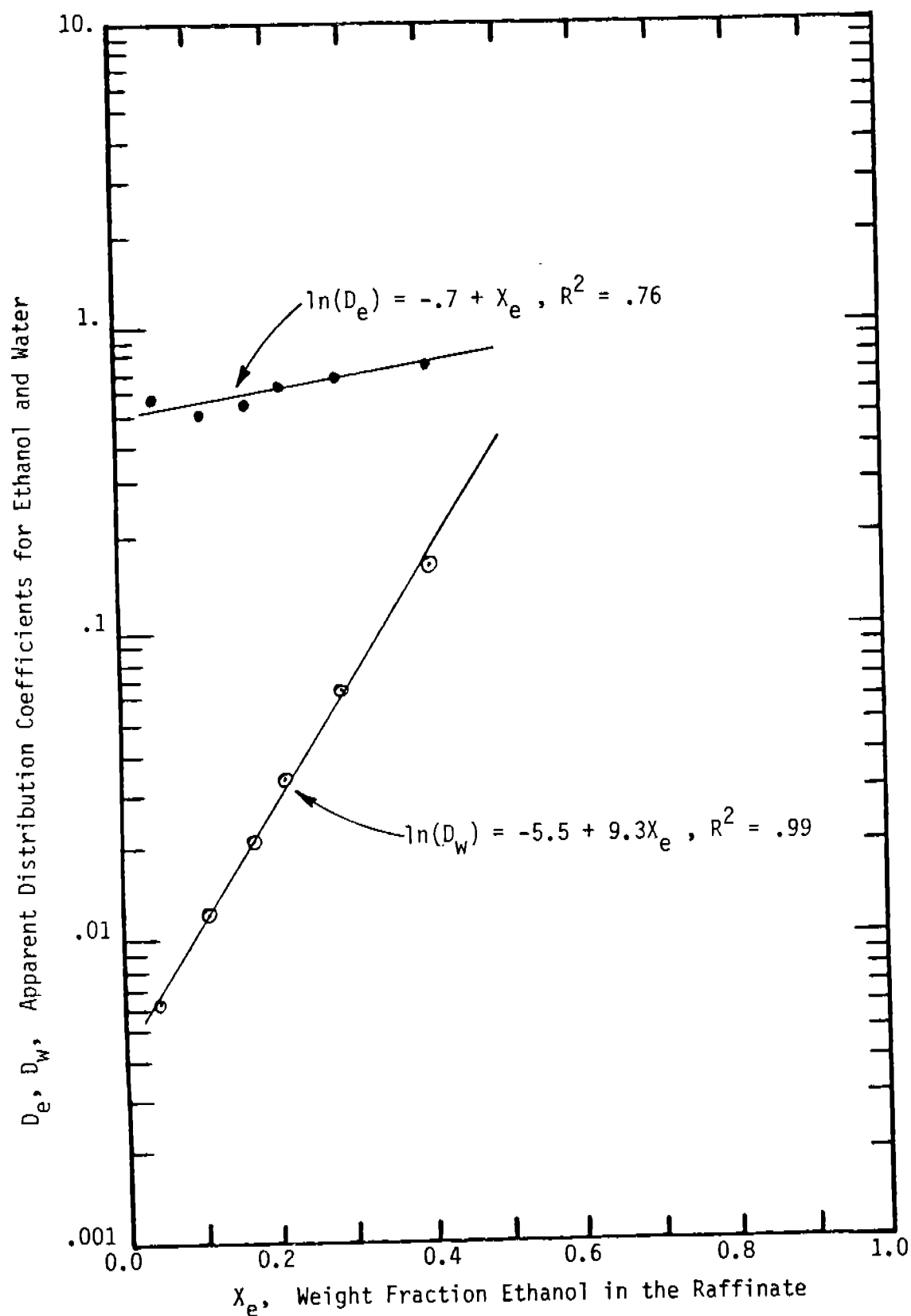
Fig. 44. Distribution coefficients for ethanol and water extraction into the solvent 25 vol % decyl alcohol, 50 vol % 2-ethylhexanol, and 25 vol % NORPAR-12.
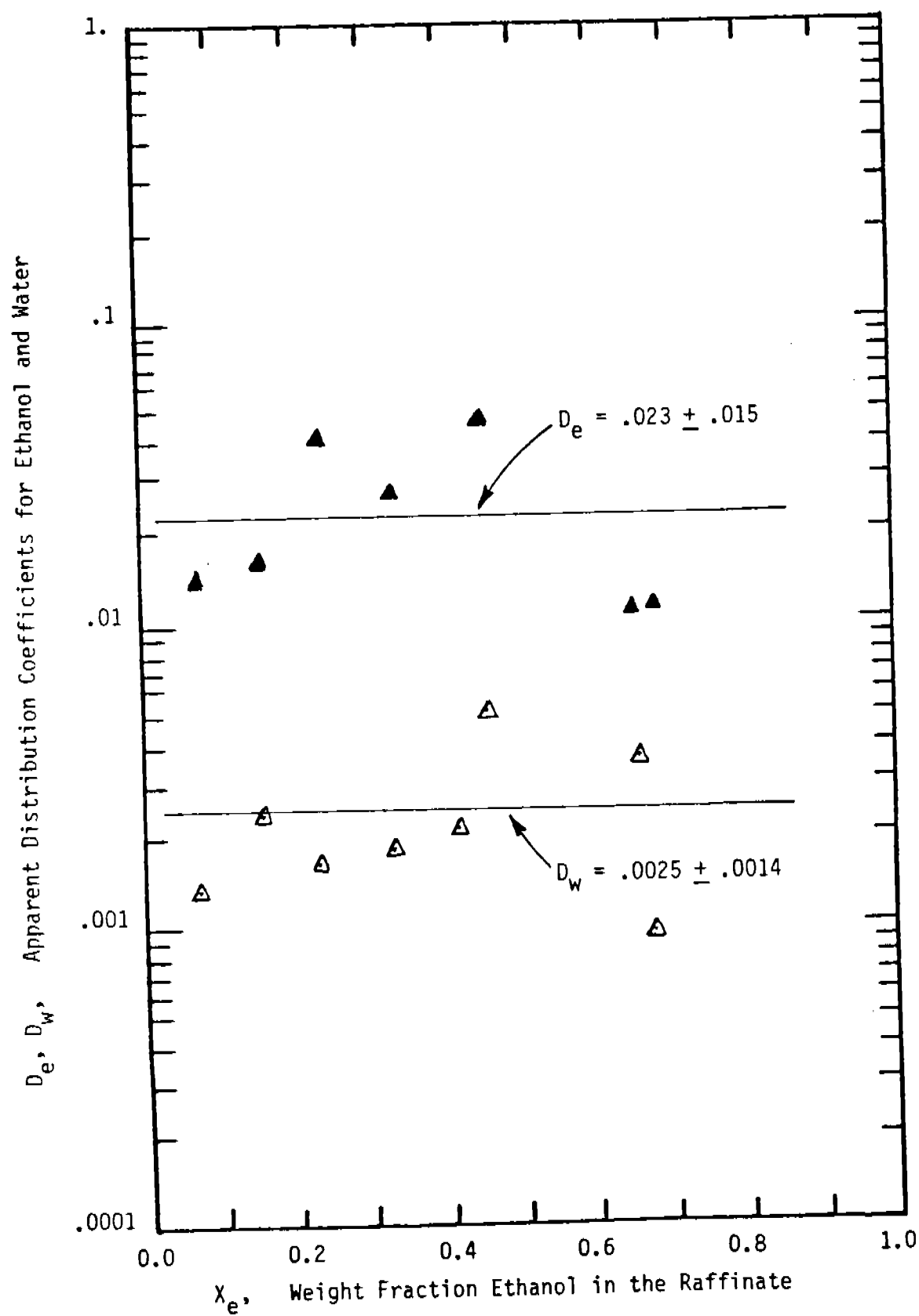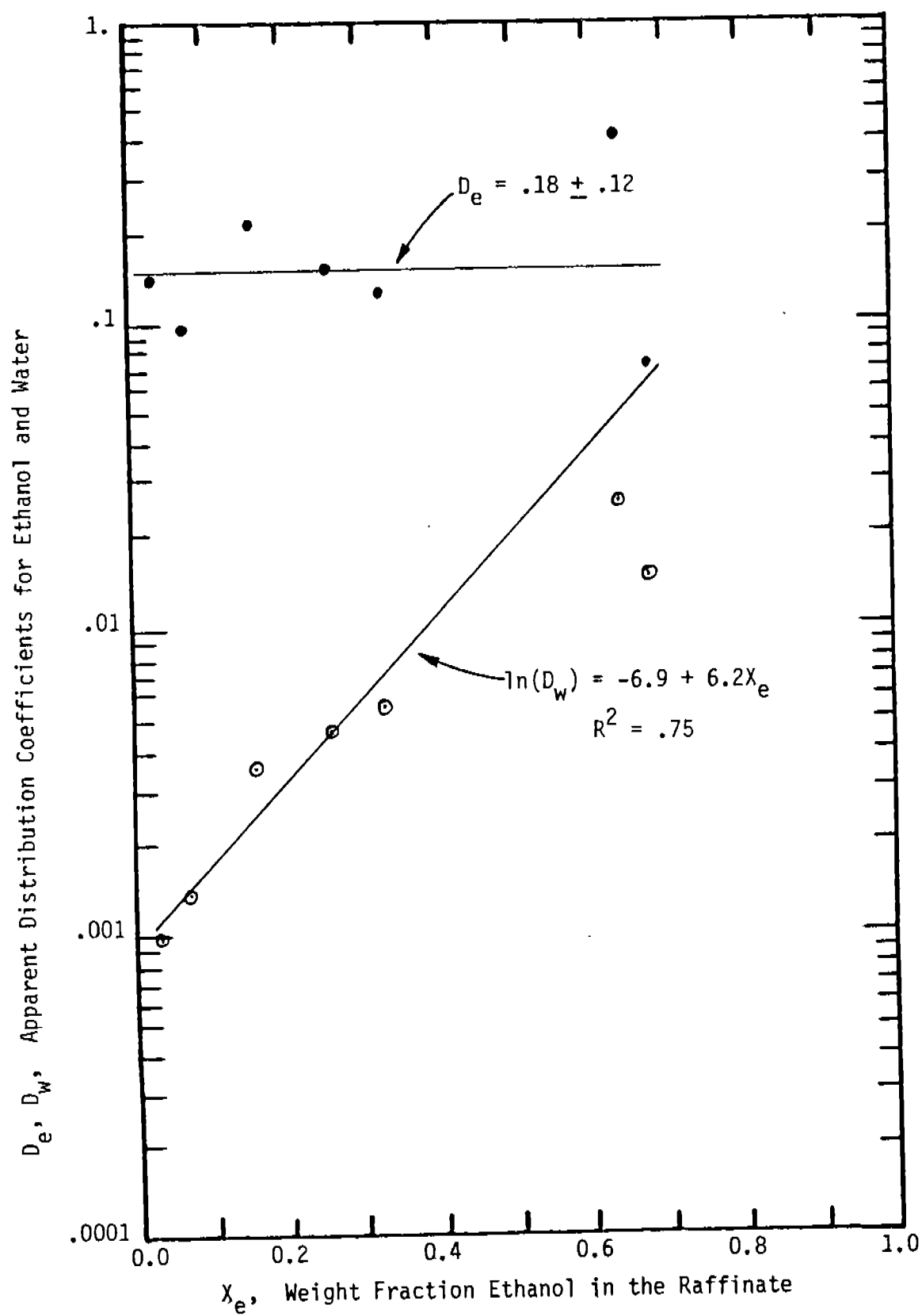
Fig. 45, Distribution coefficients for ethanol and water extraction into unleaded gasoline.

On the other hand, data obtained by an individual experimentor often tend to appear more regular and suggest that a slight dependence on the raffinate ethanol concentrations may exist (e.g. Figs. 27, 30, 32, 35, 36, 38-39, and 40-44) for some ethanol distribution coefficients. Statistically, however, the correlation coefficients for models that assume such a relatiorship exists are often have been relatively low. In such cases it may not be possible to reject the hypothesis that the ethanol distribution coefficient is independent of the ethanol weight fraction in the equilibrated raffinate. That is, the ethanol distribution coefficient appears nearly constant for some solvent systems. Based on the assumption that it is constant, then one standard deviation in the ethanol distribution coefficient typically corresponds to about plus or minus 25 % of the coefficient value.

In some cases (see Figs. 36 and 38), the extraction behavior appears highly nonideal insofar as the ethancl distribution coefficients appear to decrease substantially at the higher ethanol weight fractions in the equilibrium raffinate. This characteristic, if it actually exists, is highly undesirable since it causes the solute (i.e. ethanol) to reflux in the extraction cascace. Moreover, it is difficult to explain such behavior in the context of thermodynamic equilibria and it may indicate the existence of one or more metastable chemical complexes whose formations are path dependent. In this case the system would not be truly reversible, but additional experimental evaluations are needed before such a conclusion can be reasonably drawn. The apparent variations in distribution coefficients could be the results of experimental errors.

In contrast to the experimentally measured ethanol distribution coefficients, the water distribution coefficients clearly increase with the ethanol concentration in the equilibrated organic phase for most systems and: therefore, they are generally statistically significant functions of the ethanol weight fraction in the equilibrated raffinate. This conclusion has also been suggested by other investigators (19-21) and it tends to be true for the systems that have been studied in this work. Roddy (19,20) suggested that this behavior (i.e. the water extraction characteristics) results from the preferential extraction of the ethanol-water monohydrate into the solvent system.

The apparent distribution coefficients for ethanol and water extraction that have been experimentally measured are shown in Figs. 27-45. In all cases where a correlation for the distribution coefficient is presented, the square of the correlation coefficient, R, is also presented. As already mentioned, it is frequently not possible to reject the hypothesis that the ethanol distribution coefficient is essentially constant. Because of the interactions that are believed (22-23) to occur in alcohol and water systems, however, the highly nonideal behavior (e.g. Figs. 36 and 38) that may sometimes occur should not be surprising. For example, if a complex exists (20) which is preferentially extracted into a solvent system, then the concentration of the more extractable complex might be diminshed by increasing the ethanol concentration in the aqueous phase. That is, if the activity of the preferentially extractacted species decreased as the total ethanol activity in the aqueous phase increased, then the apparent

distribution coefficient for ethanol might also appear to decrease with increasing ethanol concentrations.

It seems that entrainment effects are important for many of the solvents that have been studied. In the tie-line experiments, for example, four dram vials (about 11 mls) were used to equilibrate the phases with vigorous shaking for about one minute. Subsequently, the length of time that was required to achieve the "primary break, or rapid settling and coalescence of the bulk of the dispersed phase" (24) was measured. In addition, many of the solvent systems exhibited a haze or fog of very small droplets in either one or both of the phases. The time to achieve the "secondary break, which represents the slow settling of the fog" (24), however, was not measured.

Many of the solvents form hazes in the organic phases which, presumably, represent water-in-oil dispersions. However, the water content of the phases at equilibrium generally increases with the ethanol content and; therefore, a hazy phase obtained from equilibration with low ethanol stock solutions (say about 10 vol %) may produce a drier ethanol product than a clear phase obtained from equilibration with a more concentrate ethanol stock solution. It is probable that the ethanol helps to solvate the water and thereby reduces, or eliminates altogether, the water haze which appears to form at the lower ethanol concentrations. In general, the driest ethanol products result from organic phase equilibrations with low (i.e. 5 to 20 vol %), rather than high, ethanol weight fractions.

The hazes which result in the organic phases are usually easily removed either by centrifugation or else by filtration through a paper filter. Although much verification is still required, it is expected that a coalescer (24), perhaps using cotton as the filtration media, will be useful to produce a crystal clear extract.

The primary break time generally increases with the ethanol distribution coefficient. That is, those solvent systems which exhibit higher ethanol distribution coefficients also tend to exhibit larger primary break times. In addition, the primary break time can become essentially infinite unless a salting agent is added to the aqueous phase. Consequently, small amounts of citric acid, about 0.5 to 1 wt %, were routinely added to the ethanol and water stock solutions. This modification results in acceptible primary break times, usually less than one minute. In the absence of a salting agent, stable emulsions are formed for many of the solvent systems that have been studied. Since small amounts of citric acid and other salting agents are normally present in fermentation broths, however, this modification should not be particularly objectionable.

It is clear that blended solvent systems can be adjusted so as to approach the desired extraction properties. For example, Fig. 46 shows the effects of blending various amounts of tridecyl alcohol in a normal paraffin mixture primarily consisting of 12-carbon chain isomers. This particular diluent, NORPAR-12, is produced as a refinery product by Exxon and it has physical properties which are similar to those of kerosene and n-dodecane. Its cost, however, is comparable to that of
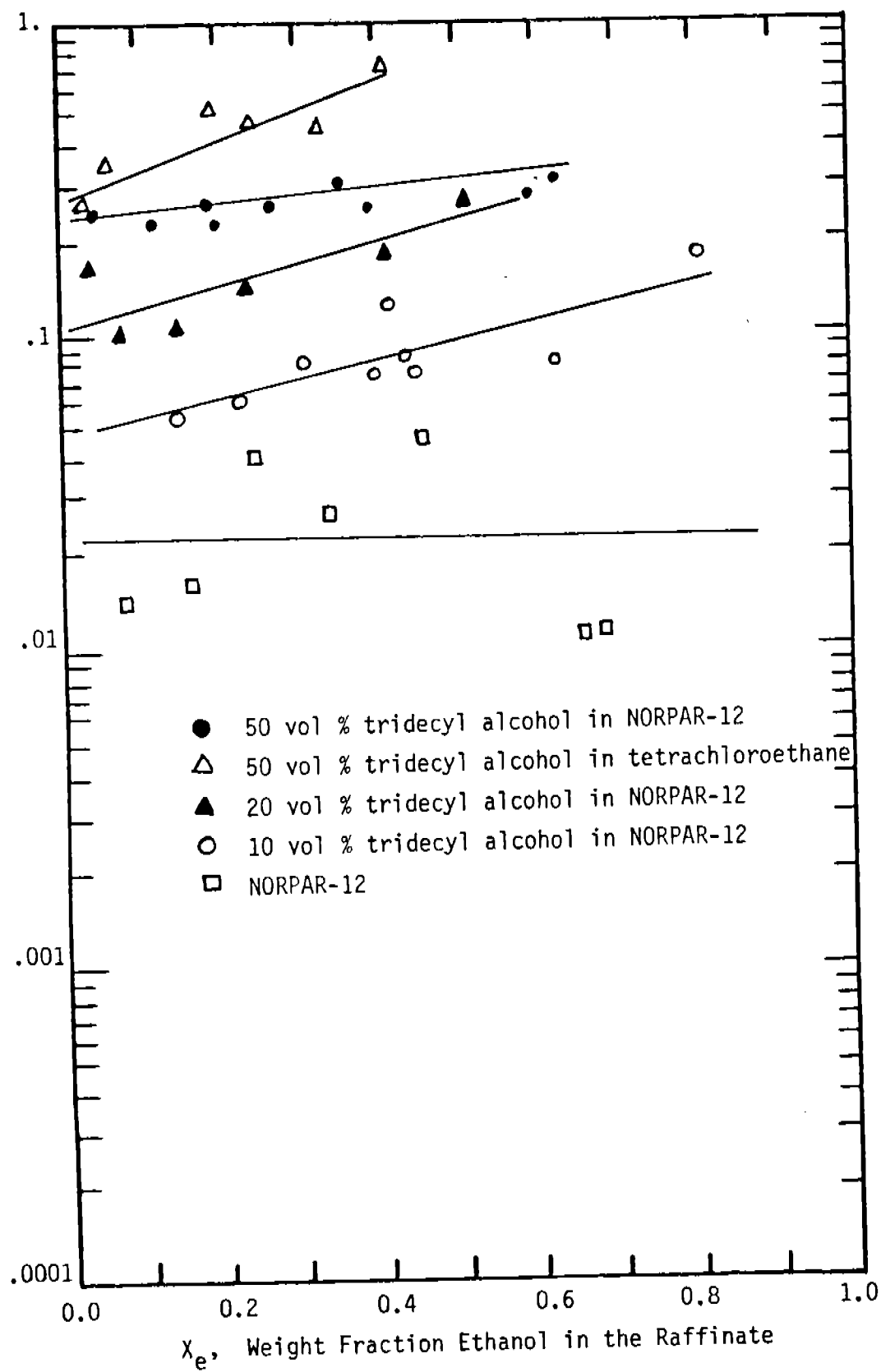
Fig. 46   Distribution coefficients for ethanol extraction into several solvent systems.
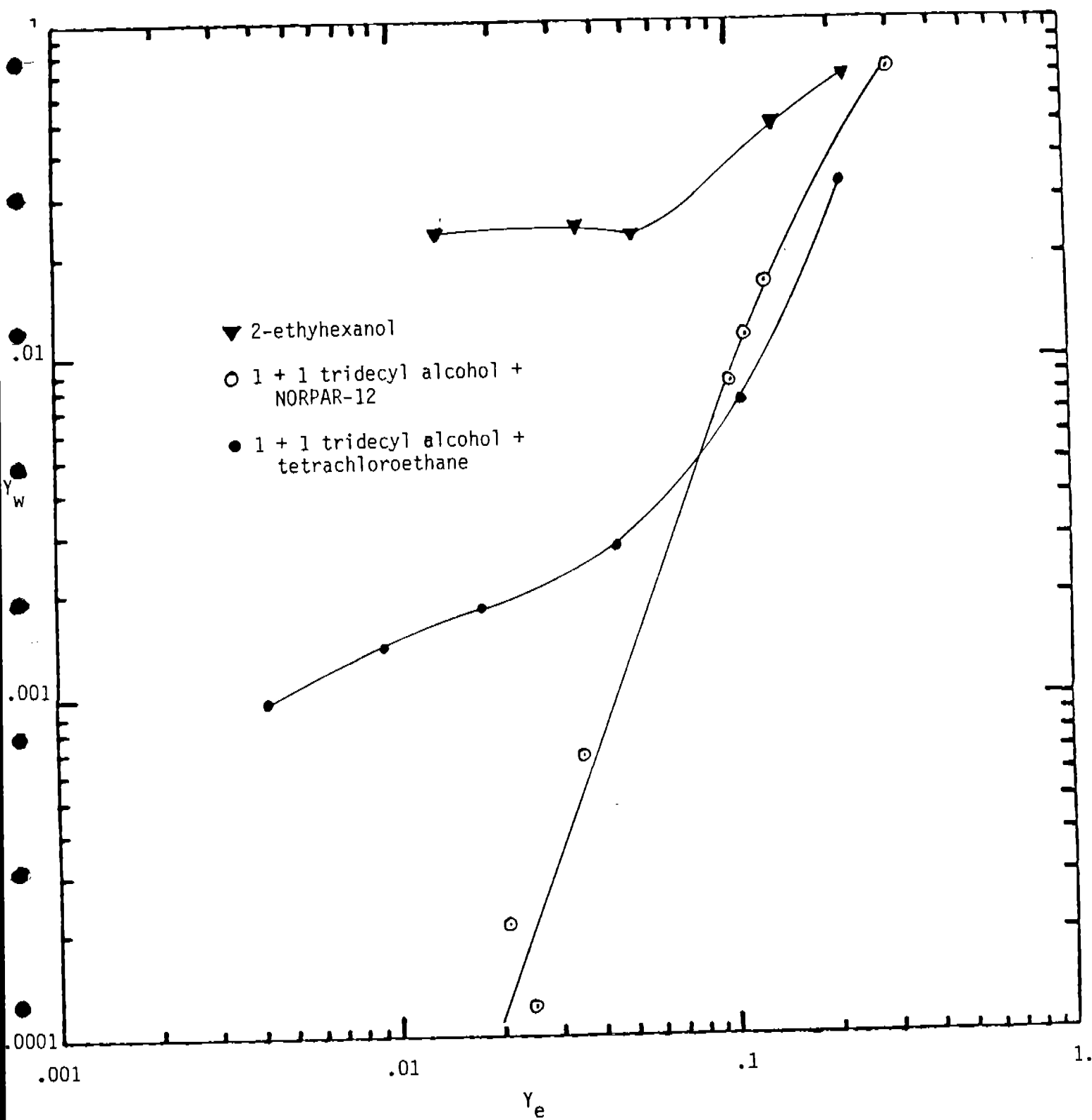
Fig. 47. Experimentally measured weight fraction of water in the organic phase, Y_w, as a function of the experimental weight fraction of ethanol in the same organic phase, Y_e.

kerosene.

As the volume fraction of tridecyl alcohol in the blended solvent is increased, the ethanol distribution coefficient is also increased as shown in Fig. 46. Pure NORPAR-12 exhibits an ethanol distribution coefficient of about 0.02 a blend of 20 vol % tridecyl alcohol in NORPAR-12 increases the ethanol distribution coefficient to slightly above 0.1 a 50 vol % tridecyl alcohol and NORPAR-12 blend exhibits an ethanol distribution coefficient of about 0.25. Hence the first incremental additions of tridecyl alcohol to the NORPAR-12 diluent yield the greatest return. The optimal blend probably contains between 20 to 50 vol % tridecyl alcohol in NORPAR-12 since the one-to-one mixture gives only a slight increase in the ethanol distribution coefficient, relative to say 20 vol % tridecyl alcohol in NORPAR-12, but the 50 % blend results in a substantial decrease in selectivity (see Fig. 48).

It can also be seen from Fig. 46 that the substitution of tetrachloroethane for NORPAR-12 as the diluent further increases the ethanol distribution coefficient at the same volume fraction of tridecyl alcohol (i.e. 50 vol %). Figure 48 and Table 8 also show that 93 the experimentally measured ethanol-to-water selectivity at 5 wt % ethanol in the raffinate is increased nearly an order of magnitude by the chlorinated diluent. Presumably, water and ethanol both compete for the extractant and the introduction of an electrophilic hydrogen bonding agent, such as tetrachloroethane, enhances ethanol extraction because that species can share its oxygen electrons more effectively than water
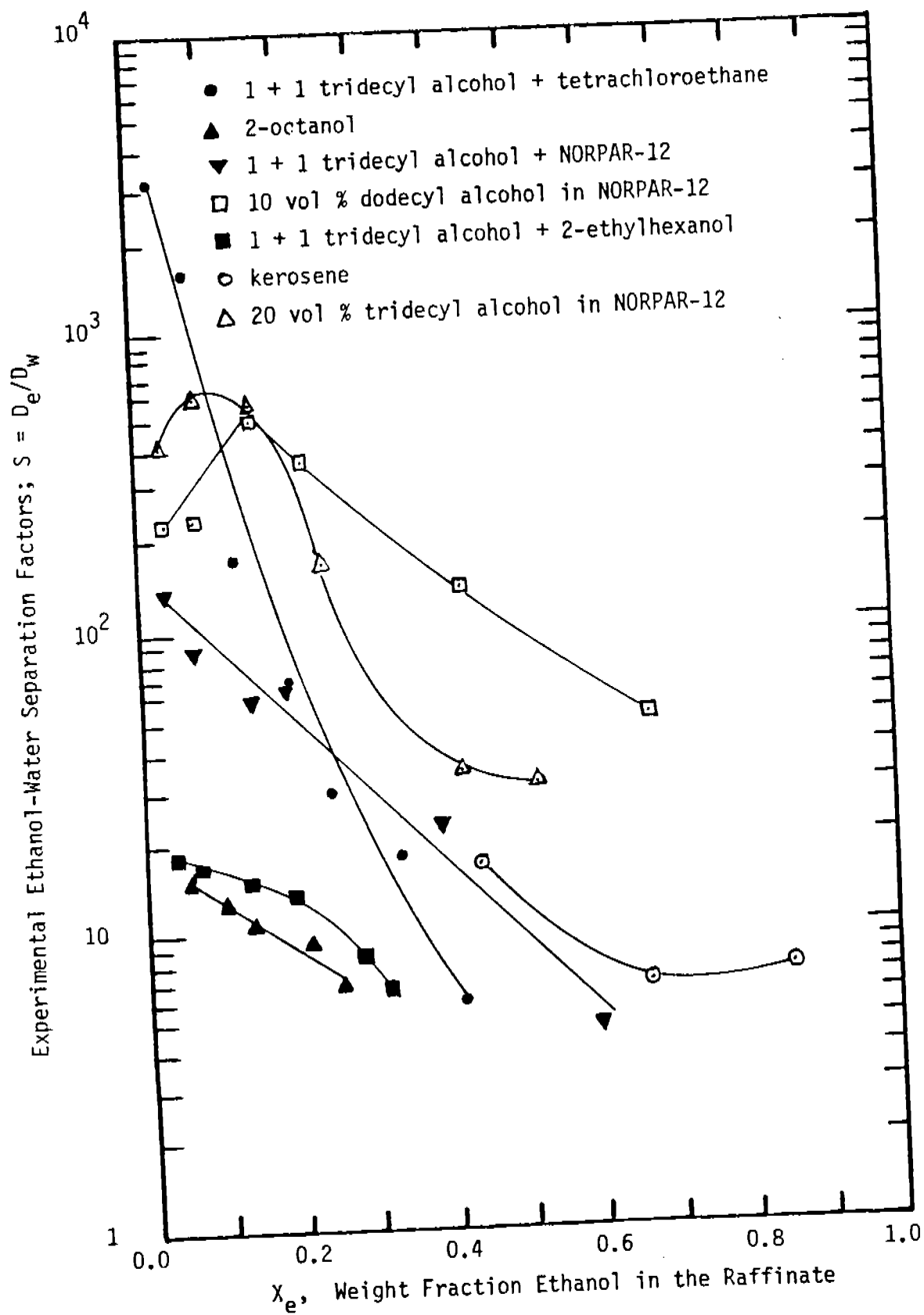
Fig. 48 Experimentally measured ethanol-water separation factors for several solvent systems.

Table 7. Extraction characteristics of unblended solvents.

Solvent Systems	$X_e = 0.05$			$X_e = 0.10$		
	S^a	De	Wt%	S^b	De	Wt%
2 - ethyl hexanol	27	0.64	59	19	0.67	68
2 - octanol	15	0.7	44	13	0.75	59
decyl alcohol	19	0.52	50	16	0.55	64
unleaded gasoline^c	133	0.18	88	98	0.18	92
kerosene	17	0.03	47	19	0.033	68
NORPAR - 12	9	0.023	32	9	0.023	50

^{a}A minimum selectivity of about 950 is required to achieve a 98 wt% product.

^{b}A minimum selectivity of about 450 is required to achieve a 98 wt% product.

^{c}Maximum of about 93wt% ethanol product can be produced.

Table 8. Diluent effects on ethanol and water extraction using tridecyl alcohol

Solvent System	$X_e = 0.05$			$X_e = 0.10$		
	S^a	De	Wt%	S^b	De	Wt%
50 vol % tridecyl alcohol in 2-ethyl hexanol	19	0.44	50	16	0.5	64
50 vol % tridecyl alcohol in 2-octanol	31	0.6	62	24	0.6	73
50 vol % tridecyl alcohol in NORPAR-12	130	0.25	87	93	0.26	91
50 vol % tridecyl alcohol in tetracholoroethane	1097	0.29	98	493	0.33	98
70 vol % tridecyl alcohol in 2-ethyl hexanol	32	0.38	63	25	0.42	73

[a] A minimum selectivity of about 950 is required to achieve a 98 wt% product.

[b] A minimum selectivity of about 450 is required to achieve a 98 wt% product.

due to the presence of the ethyl group. In addition, the chlorinated diluent also enhances phase separation and tends to reduce the primary break time and the entrainment effects. With respect to the solvent extraction cascade operation, therefore, the addition of tetrachloroethane is clearly beneficial.

The mechanisms of ethanol and water extraction appear complex under the conditions of this study. Earlier work by Roddy and Coleman (20) suggests that the ethanol monohydrate was the primary extractable species. In their work, however, an apparatus designed specifically to minimize entrainment was used to provide a constant interfacial area between the two phases. This apparatus avoids the formation of hazes and may account for some of the experimentally measured differences between the two studies. For example, the lines plotted in Fig. 47 should be nearly linear if a single species, such as the ethanol monohydrate, 35 is primarily the extractable complex. Instead, the observed changes in slope suggest that the primary mechanisms for extraction are changing. Moreover, the measured distribution coefficients measured in this study are generally larger than those observed earlier (19,20) and the selectivities are often lower. Probably, these differences can be largely attributed to the mentioned differences in entrainentrainment. Generally, however, the trends observed in the two studies are very similar.

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The observed solvent selectivity is clearly a function of the
ethanol weight fraction in the raffinate as is shown in Fig. 48. The
highest selectivities for any given solvent blend generally occur at the
lower ethanol concentrations and the rate at which the selectivity
decreases is also a function of the solvent system. Those solvent
systems with the greater selectivities also show a greater rate of
decrease in selectivity with increasing ethanol concentrations.

Figure 49 shows the projected ethanol product compositons that can
be produced from several solvent systems, based upon the
experimentally measured tie-lines. Although the selectivities tend to
decrease with increasing ethanol concentrations (see Fig. 48), the
ethanol product quality goes through a maximum (see Fig. 49) in many
cases. These data indicate that the solvent systems: (1) 10 vol %
dodecyl alcohol in NORPAR-12, (2) 20 vol % tridecyalcohol in NORPAR-12,
and (3) 50 vol % tridecyl alcohol in tetrachloroethane are all capable
of producing a fuel-grade (i.e. 98 wt %) ethanol product. Initial
ethanol increments result in a drier producty which is presumably due to
the increased ethanol competition for the extractant and, consequently,
strips some of the water from the extract. However, as the ethanol
concentrations in the aqueous phase continue to increase, the ethanol
product quality that can be achieved eventually begins to decrease.
Probably, this latter effect results from the fact that the ethanol
helps to solvate the water in the organic phase. Hence a clear organic
phase may actually contain more water than a hazy one.
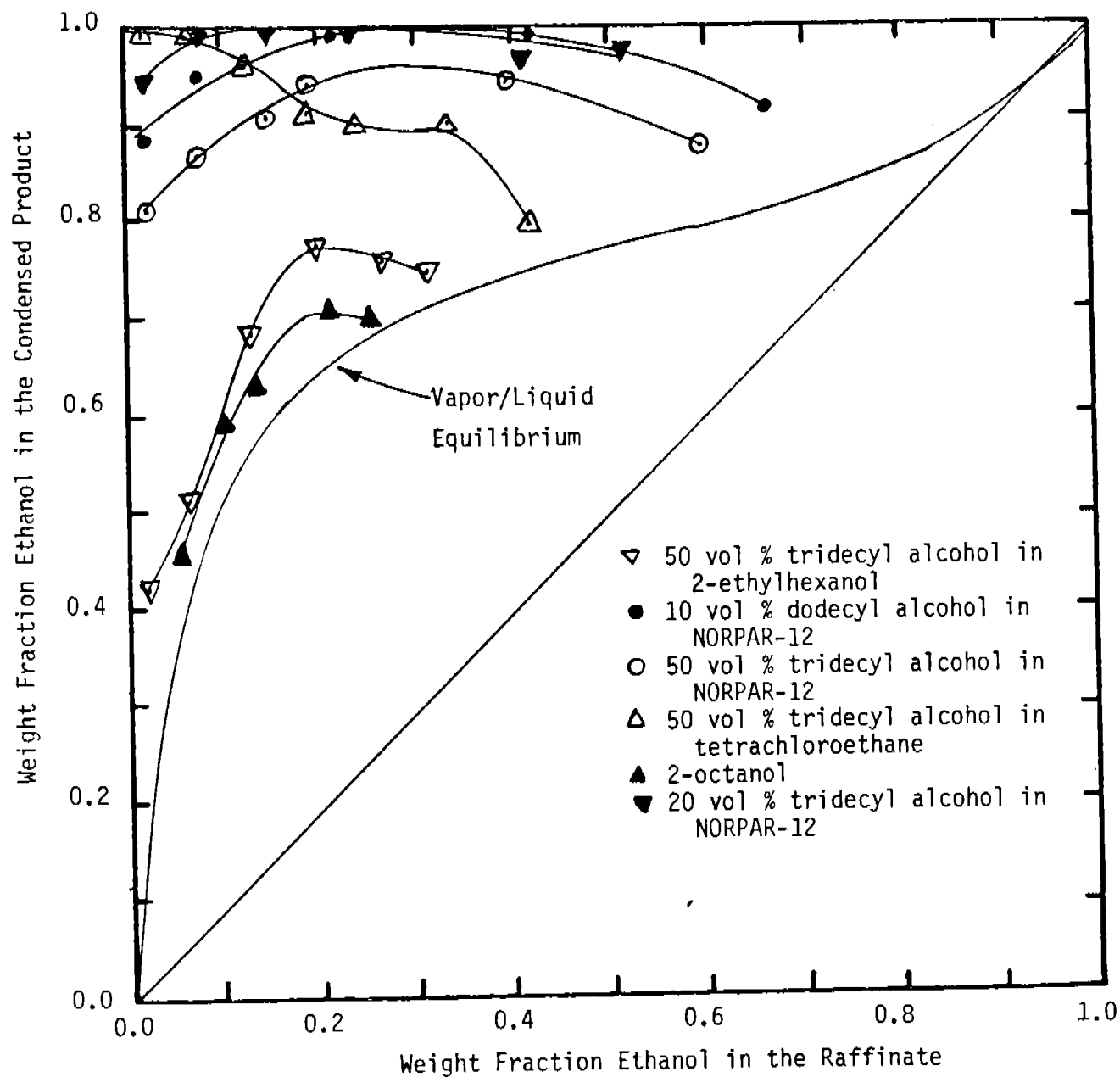
Fig. 49 Weight fraction ethanol in the condensed product after stripping the organic phase versus the weight fraction ethanol in the equilibrated raffinate (based on GC tie line analysis).

Tables 7 thru 11 are based on the experimental data, but the 1:1 distribution coefficient correlations (where applicable) have been used to smooth the individual observations. In these tables the ethanol-water selectivities, ethanol distribution coefficients, and the estimated weight percentages of ethanol in the product condensates (on a solvent-free basis) are presented at equilibrium ethanol concentrations of 5 and 10 wt % in their raffinates.

Table 7 shows the observed characteristics for several unblended alcohols and unleaded gasoline. Although unleaded gasoline has the greatest selectivity among these candidates, it appears that the driest ethanol product which could result from this solvent system is only about 93 wt % ethanol. Therefore, unleaded gasoline is not particularly useful for producing gasahol directly. In addition, its toxicity, flammability, volatility, and bad smell make gasoline less desirable as a solvent.

The selectivities of kerosene and NORPAR-12 also appear relatively low in Table 7. Although these systems are dry, the ethanol distribution coefficients are also quite low which results in low ethanol-water selectivity values.

Some of the diluent effects on tridecyl alcohol use as an extractant are summarized in Table 8. The use of NORPAR-12, rather than 2-ethylhexanol or 2-octanol as a diluent, (because the pure tridecyl alcohol is too viscous) substantially increases the observed selectivities. This effect, however, is not as dramatic as the increase

Table 9. Tridecyl and dodecyl alcohol concentration effects in NORPAR-12

Solvent System	$X_e = 0.05$			$X_e = 0.10$		
	S^a	D_e	Wt%	S^b	D_e	Wt%
10 vol % tridecyl alcohol in NORPAR-12 or kerosene	36	0.053	65	32	0.057	78
10 vol % dodecyl alcohol in NORPAR-12^c	388	0.063	95	337	0.065	97
20 vol % tridecyl alcohol in NORPAR-12	639	0.12	97	455	0.13	98
50 vol % tridecyl alcohol in NORPAR-12	130	0.25	87	66	0.26	92

[a] A minimum selectivity of about 950 is required to achieve a 98 wt % product.

[b] A minimum selectivity of about 450 is required to achieve a 98 wt % product.

[c] This system yields a 98 wt% product when equilibrated with a 20 wt% ethanol raffinate (i.e. $X_e = 0.2$).

Table 10. Effects of 2-ethyl hexanol blending on extraction behavior

Solvent Systems	$X_e = 0.05$			$X_e - 0.10$		
	S^a	D_e	Wt%	S^b	D_e	Wt%
2-ethyl hexanol	27	0.64	59	19	0.67	68
50 vol % 2-ethyl hexanol in ISOPAR-G	22	0.13	54	20	0.20	69
50 vol % 2-ethyl hexanol in tridecyl alcohol	19	0.44	50	16	0.50	64
50 vol % 2-ethyl hexanol in the Conoco diol	20	0.43	51	16	0.50	64
50 vol % 2-ethyl hexyl, 25 vol % decyl alcohols in NORPAR-12	80	0.52	81	53	0.55	85
35 vol % 2-ethyl hexyl, 35 vol % tridecyl alcohols in NORPAR-12	27	0.36	59	22	0.39	71
25 vol % 2-ethyl hexyl, 25 vol % tridecyl alcohols in ISOPAR-G	121	0.50	86	88	0.50	91

[a] A minimum selectivity of about 950 is required to achieve a 98 wt% product.

[b] A minimum selectivity of about 450 is required to achieve a 98 wt% product.

Table 11. Extraction characteristics of several phosphorous based solvents

	$X_e = 0.05$			$X_e = 0.10$		
	S^a	D_e	Wt%	S^b	D_e	Wt%
10 vol % p-dodecyl phenol in n-dodecane	31	0.081	62	27	0.081	75
30 vol % tri-n-butyl phosphate in NORPAR-12						
30 Vol % di-2-ethyl hexyl, 2-ethyl hexyl phosphonate in NORPAR-12	40	0.12	68	36	0.13	80

[a] A minimum selectivity of about 950 is required to achieve a 98 wt% product.

[b] A minmum selectivity of about 450 is required to achieve a 98 wt% product.

that is observed when tetrachloroethane is used. Unfortunately, this chlorinated solvent is relatively toxic and volatile.

Table 9 further summarizes the experimentally observed effects of changing the volume fraction of an aliphatic alcohol extractant, such as tridecyl alcohol, which has been blended with NORPAR-12. As the volume fraction of tridecyl alcohol in the blend is increased, the ethanol distribution coefficient also increases as shown in Fig. 46. The selectivities, however, are relatively low using 10 vol % tridecyl alcohol. They increase using 20 vol % tridecyl alcohol, appear to pass through some maximum value at an intermediate volume percentage of tridecyl alcohol, and then decrease when 50 vol % tridecyl alcohol in NORPAR-12 is used as the extractant. The reasons for this behavior are unclear, but they probably involve competing effects as has already been suggested.

Table 9 also shows that 20 vol % tridecyl alcohol in NORPAR-12 can be used to produce a 98 wt % ethanol product when contacted with a raffinate containing 10 wt % ethanol. The data also suggest (not shown in Table 9) that a solvent system consisting of 10 vol % dodecyl alcohol in NORPAR-12 can be used to produce a 98 wt % product when contacted with a 20 wt % raffinate at equilibrium.

The data in Table 10 suggest that the blending of ternary solvent systems may have advantages over binary blends. A simple interpretation, for example, suggests that diluting an extractant by a factor of two might reduce the ethanol distribution coefficient by a

factor of two also at the same equilibrium raffinate conditions. The data in Table 10, however, suggest that a factor of three reduction occurs when 2-ethylhexanol is diluted to 50 vol% of its maximum hydroxyl strength. On the other hand, the one-to-one blend of 2-ethylhexanol and tridecyl alcohol shows a reduction only by a factor of about 1.3 in the ethanol distribution coefficient when it is concentrated to 50 vol % of its maximum hydroxyl strength. Both the blended system 50 vol % 2-ethylhexyl, 25 vol % decyl alcohols in NORPAR-12 and the system 25 vol % 2-ethylhexyl, 25 vol % tridecyl alcohols in ISOPAR-G show significantly improved selectivities over straight 2-ethylhexanol, but only slight reductions in the ethanol distribution coefficients. Blending seems to be yielding greater improvements in these cases than might be expected based upon the behavior of their respective binary analogues.

The data in Table 11 suggest that only slight improvements may be obtained from simple binary phosphate and phosphorate extraction systems. However, ternary blends such as a phosphate or phosphonate coupled with tridecyl alcohol and NORPAR-12, for example, should probably be examined.

Some of the more favorable extraction systems have been studied by deriving correlations for the distribution coefficients based on the experimental data and performing counter current equilibrium stage calculations using the GENEX computer code. This analysis suggests that the one-to-one blend of tetrachloroethane and tridecyl alcohol, for example, can be used to recover about 98 wt % of the ethanol in a 5 wt %

Initial ethanol feed as a fuel-grade product using ten theoretical stages and an organic-to-aqueous weight ratio of about 4.7. Twenty vol % tridecyl alcohol in NORPAR-12 has been estimated to recover over 99 wt % of the ethanol in a 26 wt % feed (5) as a fuel-grade product using sixteen theoretical stages and an organic-to-aqueous weight ratio of about 7.8. Since increasing the operating temperture to about 35 degrees Centigrade is expected to increase (19) the ethanol distribution coefficients, the required organic-to-aqueous weight ratio is expected to be reduced from these estimates during actual practice.

The operating pressure of the stripper in the conceptual process is fixed by the stripping requirements for solvent recycle. As the stripper pressure is reduced, the condensation temperature of the ethanol product must also be reduced in order to control the loss of product through excessive boiling. The data in Tables 3-5 suggest that the stripper operating pressures may be as higher than 2 mm Hg, but they are probably less than 10 mm Hg. However, additional experimental measurements are needed before a design basis can be firmly established using the best blends that have been identified so far. During the next year, a new stripping apparatus will be assembled and operated. This apparatus will permit a more precise control over the temperatures, pressures, and the system material balances.

4 SUMMARY AND CONCLUSIONS

In order to develop a more attractive method than conventional distillation for drying ethanol, it is necessary to find different chemical and/or physical properties to exploit. This end may be achieved by utilizing a two-step process consisting of solvent extraction followed by vacuum distillation of the extract, for example. In this way the solvent is used to dry the ethanol product. In addition, a high molecular weight organic solvent may be chosen so that the ethanol/solvent relative volatility is significantly greater than the ethanol/water relative volatility. In other words, the original ethanol/water separation is replaced bby a solvent extraction step to separate the ethanol from water and a new ethanol/solvent vapor separation step that can be made easier by the deliberate selection of a less volatile organic solvent.

In principle, this strategy for recovering fuel-grade ethanol from dilute fermentation liquors has several advantages. First of all, the reflux requirements can be substantially reduced. Secondly, when the ethanol/solvent volatility difference is large, it is possible to greatly reduce the energy requirements of the process compared to conventional distillation. Third, since the water is rejected by solvent extraction rather than by distillation, the product dryness is not constrained by the azeotrope. Therefore, the need for a final benzene drying still may be eliminated.

A considerable amount of work is still needed to verify the
existing data; however, these preliminary results are encouraging. They
suggest that a feasible process can be developed and that it may be less
expensive to operate than conventional distillation. Despite the
experimental uncertainties that now exist, the following conclusions can
be drawn:

1. The selectivities for solvent systems generally decrease with
   increasing ethanol concentrations in their equilibrium
   raffinates.

2. The selectivities are strongly affected by the diluent. They
   are enhanced by electrophilic hydrogen bonding agents, such as
   tetrachloroethane, and they are diminished by nucleophilic
   hydrogen bonding agents such as 2-ethyhexanol.

3. Solvent blending affects both the solvent affinity for ethanol
   and its selectivity.

4. Favorable synergistic effects may occur by blending dissimilar
   alcohols such as 2-ethylhexanol, tridecyl alcohol, dodecyl
   alcohol and 2-octanol together.

5. Blended ternay solvents may exhibit favorable properties that
   are not present in their blended binary analogues.

6. Several solvent systems exist for producing at least a 98 wt %
   ethanol product including: (1) 10 vol % dodecyl alcohol in
   NORPAR-12, (2) 20 vol % tridecyl alcohol in NORPAR-12, and (3)
   50 vol % tridecyl alcohol in tetrachloroethane.

7. Chlorinated hydrocarbon diluents greatly enhance the
   selectivity of extractants such as tridecyl alcohol, but they
   probably will have limited use as solvents due to their
   toxicities and volatilities which will interfere with ethanol
   product recovery by vacuum stripping.

8. Phosphorous based extractants, such as phosphates and
   phosphonates, probably do not offer any particular advantages
   over extractants like tridecyl alcohol.

9. Any advantages for using diols and/or triols as extractants are
   diminished by their increased viscosities and tendencies to
   form third phases.

10. The class of trialkyl amine oxides probably does not offer any
particular advantages over extractants such as tridecyl
alcohol.

5 ACKNOWLEDGEMENTS

6 REFERENCES

1. D. W. Tedder and C. L. Liotta, Fuel-Grade Ethanol Recovery by Solvent Extraction, Schools of Chemical Engineering and Chemistry, Georgia Institute of Technology, Atlanta, GA (June 30, 1979).

2. D. W. Tedder, Process for Producing Absolute Ethanol without Distillation, Report of Invention, disclosed to the Georgia Tech Research Institute (October 1979).

3. D. W. Tedder, Process for Producing Absolute Ethanol by Solvent Extraction and Vacuum Distillation, Report of Invention, disclosed to the Georgia Tech Research Institute (October 1979).

4. D. W. Tedder, Process for Producing Absolute Ethanol by Continuous Fermentation, Solvent Extraction, and Vacuum Distillation, Report of Invention, disclosed to the Georgia Tech Research Institute (October 1979).

5. G. R. Cysewaski and C. R. Wilke, "Process Design and Economic Studies of Alternative Fermentation Methods for the Production of Ethanol," Biotech and Bioeng. 20 (1979) 1421.

6. D. W. Tedder and C. L. Liotta, Fuel-Grade Ethanol Recovery by Solvent Extraction, Schools of Chemical Engineering and Chemistry, Georgia Institute of Technology, Atlanta, GA (May 1, 1981).

7. E. K. Pye, personal communication to D. W. Tedder, SERI Contractors Meeting, Denver, Col. (April 1980).

8. C. Black, "Distillation Modeling of Ethanol Recovery and Dehydration Processes for Ethanol and Gasohol," CEP (September 1980) p. 78.

9. F. L. Evans, Jr., Equipment Design Handbook for Refineries and Chemical Plants, Vol. 1, Gulf Pub. Co., 2nd Ed. (1979).

10. D. F. Othmer, R. E. White, and E. Trueger, "Liquid Extraction Data," Ind. & Eng. Chem. 33 (10) (October 1941) 1240.

11. L. Alders, Liquid-Liquid Extraction, Theory and Laboratory Experiments, Elsevier NY (1955).

12. L. L. Burger, *Nuclear Science and Engineering,* 16 (1963) 428.

13. C. R. Noller and G. R. Dutton, *J. Org. Chem.,* 55 (1933) 424.

14. T. Melobendzki and A. Sachnowski, *Chemik Polski,* 15 (1917) 34.

15. J. Emsley and D. Hall, *The Chemistry of Phosphorous,* Halsted Press, J. Wiley, New York (1976).

16. D. Landini and F. Rola, *Synthesis* (1974) 565.

17. A. Brandstrom, *Preparative Ion-Pair Extraction,* Apotekarsocialenten/Hassle, Lakemedel, Sweden (1974) 145.

18. C. L. Liotta and C. M. Starks, *Phase Transfer Catalysis: Principles and Techniques,* Academic Press, New York (1978).

19. J. W. Roddy, "Distribution of Ethanol-Water Mixtures to Organic Liquids," *Ind. Eng. Chem. Process Des. Dev.* 20 (1981) 104.

20. J. W. Roddy and C. F. Coleman, "Distribution of Ethanol-Water Mixtures to Normal Alkanes from C-6 to C-16," *Ind. Eng. Chem. Fundam.* 20 (1981) 250.

21. C. R. Wilke and H. W. Blanch, *Process Development Studies of the Bioconversion of Cellulose and Production of Ethanol,* Semi-annual report to the Solar Energy Research Institute, Lawrence Berkeley Laboratory and the Chemical Engineering Department, University of California, Berkeley (April 6, 1981).

22. E. E. Tucker and S. D. Christian, "Alcohol Association Studies. 3. Vapor Pressure Measurements for the Ethanol-n-Hexadecane System," *J. Phys. Chem.* 81 (13) (1977) 1295.

23. P. L. Huyskens, M. C. Haulait-Pirson, I. Hanssens, and J. Mullens, "Water Absorption by Alcohols in Organic Solvents," *J. Phys. Chem.* 84 (1980) 28.

24. R. H. Perry and C. H. Chilton(eds), *Chemical Engineers' Handbook,* 5th edition, McGraw-Hill (1973).

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